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ARE FURTHER EXPERIMENTS NEEDED FOR DETERMIN-
ING THE ATOMIC WEIGHT OF OXYGEN ?

BY EDWARD W. MORLEY.

THE precision of experiments on the atomic weight of oxy-
gen has been gradually so much increased that, in some
cases, the mean error of a single determination is less than 1
part in 10,000.   The agreement of different series of experiments
is not so good, but if the work of different experimenters agreed
well, the question, how accurately do we really know the atomic
weight of oxygen, is not one which we can readily answer.
Neither the concordance of the experiments of a given series, nor
the agreement of the results of series of experiments by different
observers, can excuse us from search for sources of error.   All
sciences which have to do with measurement afford sufficient
instances of the fact that our conclusions are to be received with
a certain suspense of judgment.   And chemistry well illustrates
that he is wise whose assertions regard the possibility of finding
at some time evidence to the contrary.

The history of experiment on the atomic weight of oxygen
affords an interesting example of the fact that neither the con-

1 President's address, delivered before the New Haven Meeting of the American
Chemical Society.

cordance of individual observations nor the agreement of different experimenters proves that a measurement is right. Toward the middle of the century, Dumas made his classic experiments on the composition of water. The probable error of a single experiment was, in round numbers, 1 part in 400, so that the probable error of the average of the 19 famous experiments was 1 part in 2250. Now, this means that his final value was not likely to differ more than a certain small quantity from the result of the repetition of even a very large number of experiments made in the same way, with the same skill and care. But as to the difference between this result of the 19 experiments and the unknown true value, we are told absolutely nothing by the proposition that the probable error of Dumas' result was 1 part in 2250. It is a commonplace to say, that the calculation of the probable error of a series of experiments does not show how nearly the result approaches the truth, but how near it is to the result of a greater number of similar experiments. It decides, not how nearly we approach the desired goal, but whether it is useful to persevere by the present method of approach. Dumas made 19 observations, and got the value, 15.96, with a probable error of 0.007 ; that is, if he had made 100 or 1000 experiments, it is unlikely that the final result would not have been between 15.95 and 15.97, and very unlikely indeed that it would not have been between 15.94 and 15.98. But he would never have obtained a value near that which now commands confidence.

It is interesting to recall that there is hardly any instance on record where the judgment of an experimenter as to the degree of approximation to the truth attained in his work has been better justified than in the case of Dumas' classic experiments. As we all remember, towards the end of his work, there was discovered in his own laboratory a source of error, not easy to eliminate, which had affected all his determinations. The amount of the error was not a fixed quantity, and no numerical correction could be applied to the results of observation. Dumas accordingly gave to the public the uncorrected and unmodified results of experiment. But he also stated his opinion as to the degree in which his results approximated, not to the mean of a larger number of experiments of the same kind, but to the unknown and unattainable true value. He expressed the hope that his

value would be found not more than one part in 200 from the result of those subsequent experiments which should be thought satisfactory ; and it is by just 1 part in 200 that his value differs from that which is now accepted.

So the concordance of Dumas' experiments did not prove that his result was right ; neither did the agreement of experiments by different observers. Erdmann and Marchand made eight experiments by a method like that of Dumas, with some modifications. Their result was 15.973, with a probable error of 0.011. This value differs from that of Dumas by less than the sum of the probable errors, so that that agreement is perfectly satisfactory. So, also, Regnault determined the ratio of the densities of oxygen and hydrogen, from which was computed the atomic weight of oxygen as 15.963, with a probable error of 0.004. The results of Dumas, of Erdmann and Marchand, and of Regnault, show a very good agreement. But all of them, and the mean of all of them, we now know to be in error by 1 part in 200.

I adduce this example, somewhat in detail, to enforce the proposition that we must not excuse ourselves from looking for error because observations agree. We have experiments which give the atomic weight of oxygen with a probable error of 1 part in 50,000, but do we know it within 1 part in 1,000? Each individual experimenter whose work would now be regarded as free from known and tangible error, agrees fairly well with the mean of all. For instance, Noyes' results show that degree of concordance which would justify us in expecting that, if he were to make 100 or 1,000 experiments, his final mean would be as likely as not to be larger or smaller by 1 part in 9,500, and his result differs from that which we accept by 1 part in 900. So Cooke and Richards assign a value which is just as likely as not to be within 1 part in 8,000 of the result which they would have obtained by multiplying observations ; and it differs from that which we accept by 1 part in 1,500. But do we know that their means, and the means of all published results taken together, are not in error by 1 part in 900? The concordance of the results of a single experimenter, and the agreement of different experimenters, does not justify us in asserting that we do.

In determining the atomic weight of oxygen, it has been somewhat difficult to determine directly all three of the quanti-

ties involved, and so to make what Stas called a *complete* synthesis. Berzelius, Dumas, and Erdmann and Marchand, weighed oxygen and weighed water, thus determining hydrogen by difference. More recently, Dittmar and Henderson, and Leduc used the same method. Cooke and Richards, and Keiser, weighed hydrogen and weighed water, while Rayleigh and Noyes weighed hydrogen and weighed oxygen. Any proceeding which weighs hydrogen directly has a great advantage in precision ; different determinations in a given series agree better among themselves, and the series of different experimenters also agree better. But there is also a second, more important advantage. We have reason to believe that the constant errors involved in weighing hydrogen are small, for it is possible to obtain hydrogen with less than $\frac{1}{10,000}$ or even $\frac{1}{20,000}$ of its weight of impurity. There is no difficulty in weighing oxygen or water with accuracy, so if we weigh hydrogen and also weigh either oxygen or water, we may hope for a near approximation to the true value of the ratio sought.

We may hope, but we cannot *know*. We may believe that our hydrogen is pure, and that there was no error through leakage. But an unsafe stop-cock might make the apparent weight of the hydrogen in a series of experiments seem always smaller than the fact, and might yet leave the individual experiments so concordant with each other as to seem trustworthy.

If, however, we can weigh hydrogen and can weigh oxygen, and then combine them and weigh the water produced, we can at least give a better reason for our hope, if we find that the product is nearly equal to the sum of the components. The manipulation in this case is costly, and is so difficult, and involves so many minute details, that not many have patience and time sufficient for it, so that no great number of such complete syntheses has been made, and these few were made in conditions but little varied. When such complete syntheses shall have been made by different observers, with those variations of apparatus and method which may seem wise to them, we shall be able to judge of the magnitude of the errors to be feared. If such results are not concordant, we shall have much to learn as to sources of error ; but we now see some reason to expect that they will not be discordant. However, even if they are not dis-

cordant, we are not to excuse ourselves from further study of sources of error.

Before repeating determinations so troublesome, and before studying unknown sources of errors not yet detected, the experimenter should receive all possible assistance from chemical theory and from criticism. For some that criticism may be most profitable which is friendly and sympathetic ; but, for the experimenter, the value of the criticism depends on the knowledge and the acuteness of the critic. Dr. Hinrichs published, some five years ago, a criticism of all determinations and computations of atomic weights since Dumas. As is well known, he is a most strenuous and insistent supporter of Prout's hypothesis. Looking hastily through the volume, there was found, towards the end, evidence that its author was one of those who, some thirty years ago, discerned that which, in the hands of Mendeléeff, became the periodic law. It seemed possible that one who had early seen some indications of this law might, perhaps, also have discerned, even if obscurely, some principle relating to atomic weights. I therefore once spent some time and pains in carefully reading the book, and considered at length those passages, which, if any, contained valid criticism of the views which are generally accepted.

Hinrichs believes that the mean of a series of determinations of an atomic weight cannot give the true value sought. This proposition he deduces from a mathematical discussion. He believes that as larger and larger quantities are taken in our analytical operations, the results differ regularly from ideal accuracy ; sometimes the difference continually increases as the quantity taken increases; sometimes the difference increases to a maximum and then decreases again. The proper computation of an atomic weight then, according to Hinrichs, consists not in taking the mean of different observations, made with different weight of materials, but in determining the limit towards which the series converges as the weight taken decreases. A good illustration is given : we cannot determine the weight of a new coin by weighing any number of old coins ; every coin is worn and therefore light, and the mean weight of any number whatever is therefore necessarily below the mean weight of new coins. But if we weigh old coins and note the date of each, we may

take the mean weights for each year separately. If we examine coins enough, these means when plotted as the ordinates with the years as the abscissas, will give us a "fairly regular curve, lowest for the oldest coins, gradually rising towards a *limit* which they would not quite reach. This higher limit would evidently be the mean weight of the new coin."

This is an intelligible proposition. It seemed to me worth while to examine it, for to this proposition one of the most enthusiastic and most active supporters of Prout's hypothesis, a man not lacking in shrewdness or ability or learning, has entrusted the defense of his favorite belief.

He asserts that an atomic weight as determined by experiment is variable, that it depends on the amount of substance taken for the analysis or other operation, and that it varies in a continuous and regular manner. His proposition is, that an atomic weight as determined by experiment is a function of the weight of substance taken. Is there any evidence in favor of it?

I answer, first: Theory does not afford any evidence for it. Hinrichs deduces this proposition from theory by a discussion which is mathematical in form. Whether the proof is sound need not be considered, for his theory does not attempt to show the order of magnitude of the regular and continuous variations which are affirmed to depend on the weight of substance taken, and to show whether they can be separated from the irregular and discontinuous errors due to accident. We are sure that accidental errors exist; we may concede, for argument, that regular and continuous variations also exist; but this is far from implying that the actual errors in a given set of experiments will be largely or even perceptibly of the latter kind. Theory shows that there is a diurnal tide in the atmosphere; but theory does not show that the differences noted in a series of ten observations of the barometer at different hours of the day will follow the law of the diurnal tide.

But, secondly: Facts do not agree with the proposition. The accidental errors of the most precise experiments yet made are so much greater than any *systematic* variations, that nothing but accidental variations can be detected. To prove this, let us consider Stas' synthesis of silver nitrate from pure silver. This is one of the most important determinations ever made; Hin-

richs has discussed it twice in his volume ; he asserts that the ratio of silver nitrate to silver found in each analysis depends on the weight of silver taken, and twice draws curves to show this. I assert, on the contrary, that the errors, which average only 1 part in 40,000, are purely accidental, and that they follow no law. This can be proved by proving that the ratios obtained depend on any other quantities selected by accident just as much as they depend on the weights of silver taken. Hinrichs plots the results of the ten determinations, using for abscissas the weights of silver taken, and so obtains tolerable curves. I plotted the same ten observations, using for abscissas not the weights of silver taken but ten numbers selected by *sortes Virgilianae*, and get curves quite as tolerable as before ; and this I did with ten different sets of abscissas, all selected by pure accident. Now, quantities which depend on any one of eleven sets of abscissas, ten of which are selected by accident, are themselves accidental in their variations, and the variations follow no law. So far as the facts are examined, they give no evidence in favor of Hinrichs' proposition ; we have seen that theory is equally chary of her support, and we may safely dismiss the suspicion that any source of systematic error can be detected in deducing atomic weights from the means of good experiments.

Within the limits of convenience, it is well to vary the amount of substance taken in analytical determinations. This has been a frequent practice in the finest investigations. But that this practice derives any support from the so-called "limit method" cannot be conceded.

This criticism, this attempt at a theory, then, removes no obstacles and reveals no threatening pitfalls. If we desire a firmer foundation for our system of atomic weights, we must simply enlarge the experimental basis of our knowledge.

If it is only by further experiment that we can make surer of the atomic weight of oxygen, we are to consider what kind of experiments is most desirable. It is chiefly for the sake of eliciting discussion on this point that the subject of this address has been chosen.

Our present value for the ratio between oxygen and hydrogen rests on one single chemical combination, and upon two processes for determination. The first is, the synthesis of water from its

components. The second is, the determination of the densities of the gases and of their volumetric ratio. Let us consider these in order.

What synthetic experiments should be repeated? We are met by the fact that a complete synthesis, in which hydrogen and oxygen and water are all three weighed, can be made with errors only about one-fourth as large as the errors in any of the syntheses where only two substances are weighed out of the three concerned. Other things being equal, then, this process is by far the most promising. But, so far it has been carried out adequately by only one experimenter. Conditions were varied somewhat, it is true, but by no means so much as they would be varied if the same person repeated the experiments after an interval of years; by no means so much as if others were to undertake such complete syntheses. Lately, Keiser has devised a process which varies in many particulars from that already executed; it is very desirable that he should make a series of experiments, after adequate study of sources of error and of means of avoiding them. It is also desirable that, if possible, the original process of complete synthesis should be repeated with the little modifications which time is sure to introduce. These two would be enough, as far as synthesis is concerned; unless, indeed, through the invention of another process by a third experimenter, we could have still more. Other syntheses of water than by a *complete* synthesis seem less likely to be of much service, except as a school of experimentation.

What further work is desirable on the ratio of densities and of combining volumes of hydrogen and oxygen? Three constants are involved: the density of oxygen, the density of hydrogen, and the volumetric ratio.

The density of oxygen is known with a probable error of about 1 part in 50,000. It is very probable that no number whatever of further determinations would change this value by 1 part in 10,000. No further work upon this density seems at present desirable, except that whoever determines the density of hydrogen cannot well fail to determine that of oxygen also.

The density of hydrogen demands further experiment. It is possible to make, by some one of three or four slightly different processes, a series of experiments whose average variation shall

be less than 1 part in 3,000, or 5,000, or even 10,000 ; but dif-
ferent series do not agree sufficiently with each other.   We are
far from knowing the density of hydrogen so well that more
observations might not change our value by 1 part in 2,000 or
3,000.   It is very desirable that further observations should be
undertaken by at least two different methods.   In one method,
hydrogen should be weighed while absorbed in palladium, should
be then transferred to a measuring apparatus without the use of
stop-cocks, and should be there measured.   This process should
be repeated with measuring apparatus of varied volumes.   In
another method, hydrogen should be weighed after Regnault's
method, in a counterpoised globe, but with such precautions
that leakage through a stop-cock, and contamination with vapor
of mercury, should be excluded.   The globe should be exhausted
till the remaining air is a small fraction of a millionth, should be
sealed off from the pump, and should be connected with a con-
denser at the temperature of liquid air, so as to remove mer-
curial vapor.   After this hydrogen is to be admitted without the
use of stop-cocks.   The manipulation is not difficult, and the
method would confirm the results of the previous method.

The ratio of the combining volumes of hydrogen and oxygen
is not known with the degree of confidence which is desirable.
The history of the matter is not an interesting one.   Further
continuance of the two series of experiments on which the pres-
ent value depends would be most unlikely to change it by 1 part
in 10,000, for its probable error is 1 part in 40,000.   But one of
the experimenters has obtained results differing from that finally
adopted by as much as 1 part in 220.   The other experimenter
has entirely discarded the result of one series and replaced it,
not by a better series of the same kind but by one of a quite
different nature, not carried to its proper completion, and accord-
ingly reduced by the use of the constants of van der Waals'
equation.   It is desirable that experiments be made to furnish
means for a new reduction by measuring the change of volume
when 2 volumes of hydrogen and 1 volume of oxygen are mixed,
being at the same pressure before and after mixing.   This
experiment has lately been made by Berthelot, whether with
sufficient precision for the purpose is not known at this moment.
It is also desirable that the ratio of the combining volumes of

oxygen and hydrogen should be measured with the gases contained in vessels of the dimensions of those used for obtaining their densities.

If these syntheses and these studies of ratios of densities and combining volumes should agree as well as it is safe to expect, we should know the atomic weight of oxygen as confidently as we can know it while the value rests on a single chemical process, the combination of the two gases to form water.

But this is not so much as is desirable. We know the atomic ratio between silver and oxygen with considerable confidence, because this rests not on a single chemical process but on eight different chemical processes, which give eight independent results, and because these eight results agree. Is there, then, any chemical process by which the atomic ratio of oxygen and hydrogen can be determined, other than the analysis or synthesis of water ? Is there any element whose atomic ratio to oxygen is well known, whose ratio to hydrogen is capable of accurate direct determination ?

It is probable that, given an adequate equipment, the direct ratio of hydrogen to chlorine, of hydrogen to sodium, of hydrogen to magnesium, or of hydrogen to aluminum, could be determined with sufficient precision for the purpose, provided that the ratio of chlorine to oxygen, of sodium to oxygen, of magnesium to oxygen, and of aluminum to oxygen are well enough known. This may not now be the case with aluminum or magnesium, but is the case with chlorine and with sodium, whose atomic ratios to oxygen may be fairly assumed to be known within 1 part in 2,500. If, now, we can determine the ratio of chlorine to hydrogen, or of sodium to hydrogen, to 1 part in 5,000, we could compute, by a new method, the ratio between hydrogen and oxygen. If this should agree with the present value, within some such quantity as 1 part in 2,000, we should be as confident of the truth of our value of the atomic weight of oxygen as we can well hope to be.

The difficulties in making a complete synthesis of hydrochloric acid are not small, nor are they all well understood. Some unexpected circumstance may be prohibitive. But there is good reason to hope that 3 or 4 or 5 grams of hydrogen could be

weighed, that a nearly equivalent quantity of chlorine could also be weighed, that the two could be combined, and that the product could be weighed.   One serious difficulty would be found in attempting to prepare pure chlorine, but the difficulty does not seem insuperable.   The manipulation of the corrosive element requires invention, but seems not difficult.   For the collection of the hydrochloric acid in a weighable form, there seem to be alternative methods, not very troublesome of execution, unless unforeseen difficulties are encountered.   If the ratio between hydrogen and chlorine could be determined to 1 part in 5,000 or to 1 part in 10,000, it would be a very interesting addition to our list of known constants, most helpful in establishing confidence in the ratio between oxygen and hydrogen.

So, also, if sodium can be prepared of sufficient purity, or of sufficiently constant impurity, it seems possible to weigh 100 or 200 grams, to act on it with water in such a way as to produce a slow evolution of hydrogen, and to determine the weight of this hydrogen by loss.   Whether sodium can be obtained sufficiently free from absorbed hydrogen and whether it can be prepared for weighing without attacking the vessels which contain it, are questions which need further experiment.   It is probable that a vessel of platinum-iridium alloy could be made which would make success almost certain, but at considerable cost.   In this case also, if the ratio between sodium and hydrogen can be determined to 1 part in 5,000, or 1 part in 10,000, the result would inspire confidence, or, if it must be, distrust, in our present value for the ratio between oxygen and hydrogen.

These suggestions, necessarily tentative in their nature, are submitted to the American Chemical Society, in the hope of obtaining from those who do me the honor to listen to them or to read them, expressions as to the desirability of making experiment in the lines described, and discussions of the new methods indicated as possible.

A PRELIMINARY STUDY OF THE COBALTICYANIDES.

BY E. H. MILLER AND J. A. MATHEWS.

S EVERAL years ago during the course of an investigation of the ferrocyanides of zinc and manganese,[1] it was suggested that a study of the reactions between potassium cobalticyanide and solutions of metallic salts might be of interest and that, possibly, this compound might be found useful as a reagent in either qualitative or quantitative analysis. A careful search through the literature showed that the subject had not been thoroughly investigated; that the cobalticyanides of many metals were unknown and that the properties, especially the solubilities, of the known cobalticyanides were but incompletely recorded. Apparently no work has been done on these compounds for many years, while most of the investigations bear dates prior to 1857.

The general procedure adopted in this work was:

First.—To try the action of a half-normal solution of potassium cobalticyanide[2] on half-normal solutions of all the common metals. They were first added to each other in equal quantities and the filtrate tested to see which reagent was in excess; and, having found the amount of potassium cobalticyanide needed to precipitate a given metal, to work in subsequent experiments with quantities which gave a slight excess of the precipitant. Although these solutions were only approximately half-normal, they were made with sufficient care to distinguish in the resulting precipitates between a normal cobalticyanide and a double potassium-metallic cobalticyanide. The indications show that in nearly every case a normal salt is produced by a reaction of simple double decomposition.

Second.—The solubility of the precipitates so obtained was tested in every instance in nitric, hydrochloric, sulphuric, acetic, and oxalic acids, in ammonium hydroxide and caustic potash; in all cases both cold and hot.

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[1] This Journal, 19 547 (1897).
[2] Based on the hydrogen equivalent in grams per liter.

These tests were made by adding the acid or alkali to the original liquid containing the precipitate, and, in each instance, an amount of solvent equal in volume to the original liquid was employed. A few precipitates were filtered and their solubilities tested in concentrated acids.

The special solutions used were of the following strengths:

$K_3Co(CN)_6(N/2)$ 55.52 grams per liter.

HNO_3	(1 : 3)	sp. gr.	1.135 = 22 per cent.	
HCl	(1 : 1)	" "	1.10 = 20 " "	
H_2SO_4	(1 : 4)	" "	1.20 = 28 " "	
$HC_2H_3O_2$		" "	1.03 = 22 " "	
$H_2C_2O_4$	saturated solution		= 10± " "	
NH_4OH	(1 : 2)	sp. gr.	0.96 = 10 "	" NH_3.
KOH		" "	1.11 = 10 "	" K_2O.

No highly colored or characteristic precipitates have as yet been found which can be employed as indicators to show an excess of potassium cobalticyanide, nor do the precipitates settle readily enough to allow this point to be determined by cautious additions of cobalticyanide to the clear supernatant liquid or by spot tests. In every precipitation the potassium cobalticyanide was added to the metallic salt solution and the presence of either substance in excess had usually to be determined in a few drops of the filtrate from the resulting precipitate. The experimental part of our work will show that, in general, the cobalticyanides insoluble in water, are also insoluble in and unaffected by acids, but are soluble in or decomposed by alkalies. None of them are decomposed by boiling as is the case with several ferricyanides. There is little similarity in either solubility or appearance between the corresponding ferri- and cobalticyanides. The metals except those of the alkalies and alkaline earths were taken up in their qualitative sequence, beginning with the silver-lead-mercury group.

Silver Cobalticyanide.—When equal volumes of half-normal silver nitrate and potassium cobalticyanide solutions are mixed, the silver is completely precipitated as silver cobalticyanide, a white curdy precipitate, which settles and filters well; is insoluble in all the acids used, being transposed by hydrochloric acid; is soluble in ammonia and decomposed by potassium hydroxide giving a precipitate consisting mostly of silver oxide.

Lead Cobalticyanide.—Neither lead acetate nor nitrate are precipitated by potassium cobalticyanide, either in neutral or acid solutions. Zwenger[1] made it from lead carbonate and cobalticyanhydric acid. This salt, crystallizing in laminated crystals containing 4 molecules of water, he says, is soluble in about 3 parts of water from which solution it is precipitated by ammonia as a basic salt.

Mercurous Cobalticyanide.—Mercurous nitrate gives with potassium cobalticyanide a white, flocculent precipitate, which settles quickly. It was therefore possible to use concentrated ammonia as an indicator. Spot tests on porcelain showed a black precipitate as long as there was an excess of mercurous nitrate. Mercurous cobalticyanide is transposed by hydrochloric acid and seems to be partly changed by hot sulphuric acid but not by oxalic acid. It is unaffected by nitric and acetic acids, but decomposed by alkalies. Mercurous cobalticyanide is probably a normal salt, having the formula, $Hg_3Co(CN)_6$.

Mercuric Cobalticyanide is unknown. There is no precipitate formed when potassium cobalticyanide is added to mercuric chloride either in neutral or acid solution.

Arsenic, in hydrochloric, sulphuric, or ammoniacal solution gives no precipitate.

Antimony in a solution sufficiently acid to prevent the precipitation of a basic salt, gives no precipitate.

Stannous salts in neutral, acid, or potassium hydroxide solution are not precipitated by potassium cobalticyanide. Gmelin[2] states that stannous but not stannic salts are precipitated, but does not give the conditions under which he obtained the precipitation.

Cupric Cobalticyanide.—When a solution of copper sulphate is completely precipitated by potassium cobalticyanide solution, there results a turquoise-blue compound. This salt, apparently $Cu_3Co_2(CN)_{12}$, is insoluble in all acids, cold or hot; very soluble in ammonia, and with caustic potash it turns green, becoming darker and darker until black cupric oxide separates. The ammoniacal solution upon evaporation gives small shining blue crystals to which Zwenger,[3] who first worked with this

1 *Ann. Chem.* (Liebig), 6a, 158.
2 "Handbook of Chemistry" (1852), Vol. VII, p. 495.
3 *Loc. cit.*

compound, assigns the formula $Cu_3Co_2(CN)_{12} . 2NH_3 . 5H_2O$.

Cuprous Cobalticyanide, of which no mention is found in the literature, results from the precipitation of cuprous chloride by means of potassium cobalticyanide. It is a faintly yellow precipitate which filters badly; it is insoluble in acids and cold ammonia but soluble in hot, dilute ammonia. It is partly decomposed by potassium hydroxide in the cold and completely when hot. It is slowly oxidized by nitric acid, giving the blue cupric cobalticyanide.

Bismuth Cobalticyanide.—A solution of bismuth nitrate, rather strongly acid with nitric acid, is precipitated by potassium cobalticyanide giving a dense white precipitate, very soluble in hydrochloric but insoluble in the other acids and ammonia. Potassium hydroxide gives in the cold $Bi(OH)_3$, which, on boiling, may be changed to yellow Bi_2O_3. The original precipitate seems to be a normal cobalticyanide, but it has not yet been analyzed and no mention of such a compound was found in the literature.

Cadmium Cobalticyanide.—The statement appears in Gmelin's "Chemistry" (1852) that with cadmium sulphate, potassium cobalticyanide forms a brown precipitate, turning white later, soluble in excess of cobalticyanide and also in acids. In our experiments cadmium chloride was employed; the precipitate was white and amorphous, not soluble in excess of cobalticyanide nor in any acid except warm hydrochloric acid, from which it reprecipitates on cooling. To determine whether it is changed or not during this treatment will require quantitative work. It is completely soluble in cold ammonia but potassium hydroxide decomposes it, giving cadmium hydroxide.

Solutions of gold, platinum, titanium, vanadium, uranium, or zirconium are not precipitated by potassium cobalticyanide.

Aluminum chloride and chromium salts gave no precipitate with cobalticyanide. Certain double ammonio-chromic cobalticyanides have been described by Christensen[1] and by Braun.[2]

Ferric Cobalticyanide.—When potassium cobalticyanide is added to a solution of ferric chloride no precipitate forms at first, but the solution assumes a light green tint and on standing a

[1] *J. prakt. Chem.* [2], **23**, 52.   [2] *Ann. Chem.* (Liebig), **125**, 153 *et seq.*

few minutes becomes cloudy and iridescent. The precipitation increases with the formation of an amorphous yellow precipitate which runs through the filter. By boiling, it becomes canary-yellow and flocculent, filtering fairly well. The precipitation does not seem to be complete ; it is retarded by the presence of an excess of cobalticyanide or by large quantities of ammonium salts. The precipitate once formed is not soluble in cobalticyanide solution, nor in mineral acids, cold or hot, dilute or concentrated. Hydrochloric acid changes the color of the precipitate and renders it almost impossible to filter. Insoluble in acetic acid, cold or hot ; when freshly precipitated it is instantly soluble in oxalic acid but reprecipitates on boiling. It seems that at least two different compounds are produced ; they differ both in color and solubility ; the greenish one is soluble in oxalic acid and the yellow one insoluble. The latter is formed by long standing in the cold or rapidly by heating. Both give ferric hydroxide with ammonia or potassium hydroxide in the cold. If the ferric salt and the cobalticyanide solutions are mixed hot, precipitation of the yellow compound is instantaneous, no matter which reagent is in excess. The well-washed ferric cobalticyanide gives no red color with ammonium thiocyanate.

Ferrous Cobalticyanide.—Ferrous sulphate and potassium cobalticyanide seem to give a normal ferrous cobalticyanide,—a slightly yellow, amorphous, slow-settling precipitate. When an excess of cobalticyanide is present there is no oxidation or change of color in the ferrous cobalticyanide, even upon long boiling. The precipitation is complete and filters well. With nitric acid, cold and hot, and with hydrochloric and sulphuric acids, hot, there is oxidation. The precipitate darkens in varying degrees, most with nitric and least with sulphuric acid. After treatment with these acids the precipitate filters badly. No change is noticed with acetic or oxalic acids; in the presence of the latter it filters very well. With ammonia the precipitate is partially decomposed in the cold, becoming bluish, and by boiling is completely converted into ferrous hydroxide. With potassium hydroxide it gives a greenish tint, darkening on standing, becoming slate-colored by boiling, forming probably a mixture of ferrous and ferroso-ferric hydroxides.

Manganese Cobalticyanide.—This precipitate, apparently normal, is pure white and filters well. It is insoluble in all cold acids but not absolutely so in hot mineral acids. Alkalies decompose it giving first $Mn(OH)_2$ and later by oxidation, $Mn_2O_2(OH)_2$.

Zinc Cobalticyanide is formed when a solution of zinc sulphate is precipitated by potassium cobalticyanide. It is pure white, settles quickly and filters well ; insoluble in hot water, cold or hot acids, except that a trace seems to dissolve in hot sulphuric acid. This precipitate as well as a few others, *e. g.*, ferrous and ferric cobalticyanides, on boiling with hydrochloric acid passes into a condition which renders it impossible to filter even on double filters. It is very soluble in alkalies.

Cobalt Cobalticyanide.—From solutions of cobaltous chloride, potassium cobalticyanide precipitates a rose-pink, amorphous, rather gelatinous precipitate which is insoluble in cold and hot acids. At $100°$ or even lower it looses water and becomes blue. This fact was noted by Zwenger, who also states that he formed this compound by heating cobalticyanhydric acid with concentrated sulphuric acid and diluting with water before the decomposition was complete. A peculiarity of many cobalticyanides is the large amount of water which they retain after drying at $100°$ C. Zwenger noticed that the blue anhydrous cobaltous-cobalticyanide rapidly absorbs moisture from the air and that when water is poured upon it, there is a considerable evolution of heat. We found that the ferrocyanides of zinc and manganese acted in the same way. When cobaltous-cobalticyanide is treated cold with ammonia, it gives a brown solution and pink residue ; on boiling, the solution becomes pink and the residue greenish-brown. The presence of ammonium salts increases the solubility of this compound in ammonia ; it is completely soluble in concentrated ammonia. Caustic potash gives first blue basic salts and on standing or boiling rose-colored cobaltous hydroxide.

Nickel Cobalticyanide results when potassium cobalticyanide is added to solutions of nickel salts. Zwenger states that this precipitate cannot be washed free from potassium salts and that the pure nickel cobalticyanide, $Ni_3Co_2(CN)_{12}$, must be made from cobalticyanhydric acid and a nickel salt. The precipitate is

SOLUBILITES OF THE COBALTICYANIDES.

$K_3Co(CN)_6$	(1) HNO_3.	(2) HCl.	(3) H_2SO_4.	(4) $H.C_4H_3O_2$.	(5) $H_2C_2O_4$.	(6) NH_4OH.	(7) KOH.	Remarks.
+$AgNO_3$ white, curdy ppt.	(cold) i (hot) i	AgCl / AgCl	i / i	i / i	i / i	partly s / s	Ag_2O / Ag_2O	Precipitation complete. Settles and filters well. (6) White crystalline ppt. (double salt) on evaporation. Easily sol. cold conc. $NH_4(OH)$.
+$Hg_2(NO_3)_2$ white, flocculent ppt.	i / i	Hg_2Cl_2 / Hg_2Cl_2	i / i	i / i	i / i	$NH_2Hg_2NO_3$ / $NH_2Hg_2NO_3$	Hg_2O / Hg_2O	(3) Seems slightly soluble hot or else is partly changed to Hg_2SO_4. (5) Not changed to oxalate.
+$CuSO_4$ turquoise-blue ppt.	i / i	i / i	i / i	i / i	i / i	s / s	CuO / CuO	Filters well. (6) Intense blue solution, giving double NH_3 compound on evaporation. (7) Turns green, getting darker until black CuO separates.
+$Bi(NO_3)_3$ dense, white ppt.	i / i	eas'y s / s	i / i	i / i	i / i	i / i	$Bi(OH)_3$ / Bi_2O_3	Precipitation done in strongly acid solution to prevent basic salts upon dilution. (6) Not transposed to $Bi(OH)_3$.
+$CdCl_2$ white, amorphous ppt.	i / i	s / s	i / i	i / i	i / i	s / s	$Cd(OH)_2$ / $Cd(OH)_2$	Filters badly. (2) Precipitates again on cooling.
+Fe_2Cl_6 green, becoming yellow.	i / i	i / i	i / i	i / i	i / i	$Fe_2(OH)_6$ / $Fe_2(OH)_6$	$Fe_2(OH)_6$ / $Fe_2(OH)_6$	(5) When freshly precipitated and greenish it is readily sol. in oxalic cold. Ammonia salts in quantity prevent precipitation and excess of $K_3Co(CN)_6$ retards it.
+$FeSO_4$ faintly yellowish white ppt.	i / i	i / i	i / i	i / i	i / i	partly $Fe(OH)_2$ / $Fe(OH)_2$	$Fe(OH)_2$ / $Fe(OH)_2$	(1, 2 and 3) On boiling oxidize more or less to yellow ferric cobalticyanide. (6 and 7) Some oxidation to dark-colored ferroso-ferric compounds.
+$MnCl_2$ white ppt.	i / i	i / i	i / i	i / i	i / i	$Mn(OH)_2$ and $Mn_2O_2(OH)_2$	$Mn(OH)$ and $Mn_2O_2(OH)_2$	(1, 2, 3, 4, and 5) Seem very slightly soluble hot.
$ZnSO_4$ dense, white ppt.	i / i	i / i	trace / s	i / i	i / i	easily s / s	easily s / s	(4 and 5) Bump violently on boiling.
+$CoCl_2$ rose-pink ppt.	i / i	i / i	i / i	i / i	i / i	partly s / partly s	$Co(OH)_2$ / $Co(OH)_2$	(6) Solubility increased by ammonium salts. Almost completely sol. in hot conc. NH_4OH. (7) At first blue basic salts, turning again pink.
+$NiCl_2$ robin's egg blue ppt.	i / i	i / i	i / i	i / i	i / i	blue sol. s / s	$Ni(OH)_2$ / $Ni(OH)_2$	Very voluminous precipitate, which filters poorly.
NH_4, Li, Na, Mg, Ba, Ca, Sr, Pb, Hg', Sn''+IV, Cr, Al, Pt, Au, Zr, Ti, Mo salts.	No precipitates.							Solutions of salts of other metals are not precipitated by $K_3Co(CN)_6$ and other known cobalticyanides are easily soluble in water. Such cobalticyanides are usually made from an oxide or hydroxide acted upon by $H_3Co(CN)_6$.

robin's egg blue in color, very voluminous and dries up to a vitreous mass with conchoidal fracture. It is insoluble in water and acids, cold or hot ; soluble completely in ammonia, cold or hot. Potassium hydroxide gives instantly pale green nickel hydroxide.

The effect of the reagents used on the precipitates formed by potassium cobalticyanide is shown by the accompanying table. A glance at this tabulation will show several possibilities for new separations :

1. The lead salt is exceedingly soluble, while those of silver, copper, and bismuth are insoluble in either water or nitric acid. This may find an application in the analysis of pig lead, when the separation of relatively small quantities of these impurities would be much more preferable to the separation of the lead as sulphate. The separation of the bismuth can be effected either by treatment with hydrochloric acid which dissolves the bismuth cobalticyanide and leaves the copper as cobalticyanide and the silver as chloride, or by ammonia which leaves the bismuth and dissolves the copper and silver. The bismuth compound, if not suitable for weighing, can be decomposed by potassium hydroxide and weighed as Bi_2O_3 or one of the new volumetric methods may be employed for its estimation.

2. As the precipitation of ferric cobalticyanide in the cold can be completely prevented by the presence of ammonium sulphate, and probably by other compounds, it is possible to precipitate zinc, manganese, nickel, or cobalt in the presence of iron. With zinc ores containing iron and manganese, the manganese and zinc can be precipitated as cobalticyanides and then separated by treatment with potassium hydroxide, which readily dissolves the zinc cobalticyanide and leaves the manganese as $Mn_2O_2(OH)_2$.

Another possible application is in the analysis of nickel steel, where the separation from ferric iron, if sufficiently complete, would be more convenient than the method in use, based on the solubility of ferric chloride in ether. The nickel cobalticyanide after filtration can be converted into hydroxide and then dissolved in acid for the cyanide titration or for electrolysis.

These and other possible uses of the cobalticyanides are under investigation at Columbia University.

SEVENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1899.

By F. W. CLARKE.

THE year 1899 has not been remarkably prolific in determinations of atomic weight ; and comparatively few investigations have been published. The data are given in the following pages, plus an account of two memoirs which appeared in 1898, but which reached this country only after the report for that year had been printed. These memoirs, by Vandenberghe on molybdenum, and by Kölle on cerium, were issued outside of the usual channels for chemical publication, and so seem to have escaped general notice hitherto.

BORON.

An elaborate memoir upon the atomic weight of boron has been published by Gautier,[1] who worked upon four different compounds. All weights were reduced to a vacuum, and all calculations were made with the atomic weights recommended a year ago by the committee of the German Chemical Society.

First, sulphide of boron was decomposed by a dilute solution of caustic soda ; the solution produced was then oxidized by means of bromine water, and the sulphur was precipitated and weighed as barium sulphate. The results obtained were as follows :

Weight B_2S_3.	Weight $BaSO_4$.	Atomic weight.
0.2754	1.6312	11.032
0.3380	2.0004	11.081
0.3088	1.8300	11.000
0.2637	1.5614	11.050
	Mean,	11.041

The second compound studied was the carbide, B_6C. This was heated in chlorine gas to eliminate boron ; the residual carbon was then weighed directly, and afterwards burned in oxygen to reweigh as CO_2. The atomic weights given below were calculated from the weight of the carbon dioxide.

Weight B_6C.	Weight C.	Weight CO_2.	Atomic weight.
0.2686	0.0429	0.1515	11.001
0.3268	0.0512	0.1844	10.994
		Mean,	10.997

[1] *Ann. chim. phys.* (7), **18**, 352, November, 1899.

With the third compound, boron tribromide, two series of experiments were made, representing two preparations. The bromide was in each analysis decomposed by water, special precautions being taken to avoid explosive reactions; and the bromine was finally precipitated and weighed as silver bromide. The data are subjoined:

FIRST SERIES.

Weight BBr$_3$.	Weight AgBr.	Atomic weight.
3.1130	6.994	11.009
3.3334	7.490	10.981
3.7456	8.414	11.043
3.2780	7.364	11.032
4.2074	9.452	11.026
		Mean, 11.018

SECOND SERIES.

Weight BBr$_3$.	Weight AgBr.	Atomic weight.
3.3956	7.628	11.037
4.0295	9.052	11.032
3.7886	8.512	11.003
3.1711	7.124	11.026
		Mean, 11.025

With boron trichloride the analyses were conducted precisely as in the case of the bromide, silver chloride being the final product weighed.

Weight BCl$_3$.	Weight AgCl.	Atomic weight.
2.6412	9.682	10.987
2.7920	10.234	11.000
2.4634	9.026	11.043
3.4489	12.640	11.013
2.2015	8.070	10.992
2.6957	9.878	11.030
		Mean, 11.011

The mean of the values obtained from the bromide and chloride series, 11.016, is the value which Gautier proposes to adopt.

NITROGEN.

Dean[1] has continued the investigation which was reported in 1898, relative to the atomic weight of nitrogen. The ratio studied is that between potassium bromide and silver cyanide, and the value finally found is $N = 14.031$. Only an abstract of the paper has yet appeared.

[1] *Chem. News*, 80, 279.

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CALCIUM.

A paper upon the atomic weight of calcium, by T. W. Richards, was read at the meeting of the American Association for the Advancement of Science in August, but has not, at the date of this report, been fully published. Five analyses of carefully purified calcium chloride were made to determine the ratio $CaCl_2 : 2AgCl$. Calculated with $O = 16$ and $Cl = 35.455$, the values found for Ca range from 40.121 to 40.130, the mean of all being 40.126.

NICKEL.

The work of Richards and Cushman upon the atomic weight of nickel, noticed in the report of 1897, has been continued.[1] The sublimed bromide was reduced in hydrogen, giving the ratio between bromine and the metal. The weights corrected for known impurities, and the values found, are as follows:

Weight NiBr$_2$.	Weight Ni.	Atomic weight.
2.83325	0.76081	58.705
3.21625	0.86358	58.696
2.31241	0.62094	58.703
2.87953	0.77330	58.710
2.29650	0.61679	58.719
2.98893	0.80272	58.714
5.51291	1.48056	58.716
2.24969	0.60415	58.710
	Mean,	58.709

All weights represent reductions to vacuum, and the antecedent values used in calculation are $O = 16$, and $Br = 79.955$. The complete agreement with the former determinations is almost startling. A full discussion of earlier determinations is given at the close of the paper, and it is shown that the work of Winkler and of Zimmermann is in accord with the new data.

COBALT.

Just as in the case of nickel, Richards and Baxter have extended their observations upon cobalt,[2] and now give three series of new determinations dependent upon the reduction of bromide to metal. In the first series, which is preliminary, a slight impurity is stated as "residue;" in the other series corrected weights are

[1] *Proc. Amer. Acad.*, 34, 327, February, 1899.
[2] *Ibid.*, 34, 351, February, 1899.

given.   The nature of the impurity, however, is fully discussed in the paper.

FIRST SERIES.

Weight CoBr$_2$.	Weight Co.	Residue.	Atomic weight.
5.59216	1.50873	0.00193	59.007
4.61944	1.24807	0.00426	58.996
3.75291	1.01713	0.00793	58.989
3.00645	0.81409	0.00510	59.007
		Mean,	59.000

SECOND SERIES.

Weight CoBr$_2$.	Weight Co.	Atomic weight.
5.32194	1.43428	58.996
7.50786	2.02321	58.989
2.32630	0.62677	58.973
7.44694	2.00736	59.011
	Mean,	58.992

THIRD SERIES.

Weight CoBr$_2$.	Weight Co.	Atomic weight.
5.10891	1.37721	59.016
6.41339	1.72850	58.999
6.59805	1.77876	59.021
3.02854	0.81606	58.982
	Mean,	59.004

The mean of the second and third series is 58.998, when $O = 16$ and $Br = 79.955$.   Vacuum weights are given throughout.

In a still later paper[1] Richards and Baxter check their determinations of the atomic weight of cobalt by experiments upon the chloride and oxide.   The chloride was reduced in hydrogen to metal, and the data obtained, after corrections for known impurities and reduction to a vacuum, were as follows:

Weight CoCl$_2$.	Weight Co.	Atomic weight Co.
4.16483	1.89243	59.053
2.30512	1.04723	59.035
	Mean,	59.044

The reduction of cobalt monoxide in hydrogen was similarly effected, but with varying results depending upon differences in the conditions of the experiments.

First, three determinations, with vacuum weights, gave as follows:

[1] *Proc. Amer. Acad.*, **35**, 61, August, 1899.

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Weight CoO.	Weight Co.	Atomic weight Co.
7.04053	5.53779	58.962
6.69104	5.26312	58.974
7.83211	6.15963	58.927

| | | Mean, 58.954 |

These data, which are not sufficiently concordant among themselves or with the bromide determinations, probably indicate that the cobalt oxide contained some excess of oxygen. In a fourth experiment precautions were taken to avoid this difficulty, and 7.74242 grams of oxide gave 6.09219 of cobalt, whence $Co = 59.068$. In a fifth experiment, resembling the fourth, but with differences in detail, 10.58678 grams of CoO gave 8.32611 of metal, corresponding to an atomic weight of $Co = 58.929$.

The authors give elaborate particulars as to the circumstances under which each determination was made, and conclude that cobalt monoxide varies too widely in its composition to be suitable for exact measurements of atomic weight. The true value for cobalt undoubtedly lies between 58.93 and 59.07, the figure 58.995, obtained from the bromide, being the most probable.

MOLYBDENUM.

In 1897 the Belgian Academy of Sciences awarded a special Stas prize to M. Ad. Vandenberghe for his determination of the atomic weight of molybdenum. The memoir has recently been published,[1] and the data are now available.

Vandenberghe starts out with molybdenum dibromide, scrupulously purified. From this he obtains metallic molybdenum, by careful reduction in hydrogen at a white heat. The atomic weight determinations are made by the oxidation of Mo to MoO_3, by means of pure nitric acid. The product was finally dried at a temperature of from $350°$ to $400°$, and cooled in a current of oxygen. The data obtained are as follows:

Weight Mo.	Weight MoO$_3$.	Atomic weight.
0.7143	1.0711	95.851
0.3453	0.5177	95.899
0.9693	1.4533	95.889
0.5089	0.7631	95.854
1.7219	2.5820	95.855
4.2597	6.3872	95.869

[1] *Acad. Roy. des Sciences*, Mémoires Couronnés, 4to. series, Tome 56, 1898.

Reducing all weights to a vacuum, the final value becomes 95.829, when $O = 15.96$. If $O = 16$, $Mo = 96.069$. If $O = 15.88$, then $Mo = 95.349$. This value is very near that found by Smith and Maas, by an entirely different method, but rather higher than that given by Seubert and Pollard. For all practical purposes the value $Mo = 96$ may be assumed.

TUNGSTEN.

Two investigations relative to the atomic weight of tungsten have been published from the laboratory of the University of Pennsylvania. The first one by G. E. Thomas[1] contains a record of experiments upon WO_3 and $Na_2WO_4.2H_2O$. The reduction of oxide to metal, and the reverse process of oxidation, gave figures ranging from 183.51 to 184.22 for the atomic weight of tungsten, and work along this line was discontinued. With sodium tungstate three series of dehydration experiments were made, giving the ratio between water and the anhydrous salt as the measure from which to calculate. These results also were discordant, and Thomas discards the method as unsuited to accurate determinations. The object of the paper seems to be negative, and to show that neither method employed is adequate to its purpose.

The second paper, by Professor Smith, contains a section by W. L. Hardin,[2] of similar purport to that of Thomas. Experiments were made upon the oxide, the oxychloride, barium metatungstate, and the precipitation of silver by metallic tungsten, and each method was found to be defective. Discordant results were obtained in each set of trials. The mean of all experiments upon the reduction of WO_3, and the oxidation of tungsten give approximately the value $W = 184$. This value Hardin thinks it best to accept until more conclusive determinations shall have been made.

CERIUM.

Kölle's dissertation[3] upon this element deals partly with its atomic weight and partly with other matters. His material was obtained from cerite, and was purified with extreme care. Iodo-

[1] This Journal, 21, 373, April, 1899.

[2] *Ibid.*, 21, 1017, November, 1899.

[3] Beiträge zür Kenntniss des Cers. Doctoral Dissertation by Gotthold Kölle. Zurich, 1898.

metric determinations of cerium salts gave, invariably, results which were too high, and which led him to believe that the source of error was in the accepted atomic weight of cerium, an essential factor in his calculations.

Accordingly, new determinations of atomic weight were made by the standard method ; namely, the ignition of cerium sulphate to cerium dioxide. Cerium chloride prepared from the oxide, was spectroscopically examined, and found to be free from other metals. The atomic weight data are as follows, computed with $O = 16$.

Weight $Ce_2(SO_4)_3$.	Weight CeO_2.	Per cent. CeO_2.	Atomic weight.
1.84760	1.11648	60.429	139.11
1.16074	0.70078	60.331	138.78
1.53599	0.92722	60.366	138.73
0.97196	0.58661	60.353	138.64
1.40374	0.84760	60.384	138.84
1.75492	1.05956	60.377	138.80
1.53784	0.92853	60.379	138.82
1.64233	0.99150	60.372	138.76
		Mean,	138.81

This value is lower than any of the later determinations, but agrees nearly with that of Wolf. Like Wolf, and like some other recent investigators, Kölle obtained a white ceric oxide, and he regards the colored preparations of former researches as evidently impure. Furthermore, iodometric estimations made on known quantities of ceric oxide gave good results when the new atomic weight was used in calculation, but excesses of 0.8 per cent. when Brauner's or Robinson's value was employed. So far as present evidence goes there is a presumption in favor of Kölle's determination.

PALLADIUM.

Hardin's research[1] upon the atomic weight of palladium is based upon the reduction of certain compounds in hydrogen. Neither of the salts studied had been previously applied to determinations of this character, and the results obtained are therefore of special value. They are, moreover, very concordant, and seem to be more nearly conclusive than any determinations previously made. All weights were reduced to a vacuum, and the

[1] This Journal, 21, 943, November, 1899.

calculations are based upon atomic weights given in the table of your committee for 1898.

First, diphenyl-pallad-diammonium chloride was studied. After reduction, the metal was heated in air to burn off possible free carbon, then reheated in hydrogen, and cooled in air to prevent occlusion of the former gas.

Weight of salt.	Weight Pd.	Atomic weight.
0.98480	0.28953	107.06
1.10000	0.32310	106.92
1.02820	0.30210	106.96
1.19230	0.35040	107.00
1.40550	0.41300	106.98
1.26000	0.37040	107.04
2.25510	0.66310	107.08

Mean, 107.006

The second series of determinations was made upon diphenyl-pallad-diammonium bromide, with the following results :

Weight of salt.	Weight Pd.	Atomic weight.
0.88567	0.20917	107.01
1.31280	0.31000	106.99
1.50465	0.35540	107.03
2.01635	0.47635	107.05
2.92300	0.69080	107.10

Mean, 107.036

Finally, ammonium palladium bromide was studied, giving four more determinations.

Weight of salt.	Weight Pd.	Atomic weight.
0.77886	0.18006	107.03
1.53109	0.35381	106.96
2.75168	0.63614	107.03
1.88136	0.43478	106.98

Mean, 107.00

The mean of all three series, when $O = 16$, is 107.014. 107 then, may be taken as the most probable value for the atomic weight of palladium.

RADIUM.

Madame Curie,[1] having prepared a large quantity of radiferous barium chloride, has determined the chlorine in several fractions

[1] *Chem. News,* **80,** 793.

of the material, and so ascertained the atomic weight of the metal contained in it. Three determinations gave for this atomic weight:

$$140.0$$
$$140.9$$
$$145.8$$

Hence the atomic weight of radium is higher than that of barium, although its true value is still unknown.

THE ELECTROCHEMICAL EQUIVALENTS OF COPPER AND SILVER.

This subject has been reinvestigated somewhat elaborately by Richards, Collins, and Heimrod.[1] First, copper was precipitated in comparison of the silver and copper voltameters, under varying conditions as to temperature, character of solution, and size of plates, and the results are summarized as follows for the atomic weight of copper, when $Ag = 107.93$.

Large plates, cupric solutions,			$t.$ 20°,	$Cu = 63.47$	
" " " "			$t.$ 0°,	63.525	
Small " " "			$t.$ 0°,	63.547	
Medium " cuprous "			$t.$ 0°,	63.573	
" " " "			$t.$ 60°,	63.615	
Corrected results from cupric solutions,				$Cu = 63.563$	

a value 0.041 lower than that determined by chemical processes.

A study of the silver voltameter by itself showed that it gives results which are too high by about 0.081 per cent. Correcting the atomic weight of copper in accordance with this observation, the true value is found to lie between 63.598 and 63.615. The value previously established by Richards was 63.604, a confirmation of the present work, which is to be continued.

TABLE OF ATOMIC WEIGHTS.

In the following table of atomic weights your committee give first its own set of values, based upon both fundamental standards. Next is given Richards' table, revised for 1899, and finally that of the German Chemical Society. The values in the German table are rounded off to convenient approximations for practical use; those of Richards give the nearest significant figure, and the latter policy, which is wise, has also been adopted by your committee. There are, however, slight differences of

1 *Proc. Amer. Acad.*, **35**, 123, December, 1899.

opinion in some cases as to where the nearest significant decimal place really is.   Hardin's work on palladium and tungsten, and Kölle's research on cerium, have led to the only notable changes from last year.

| | Clarke. | | | |
	H = 1.	O = 16.	Richards.	German.
Aluminum	26.9	27.1	27.1	27.1
Antimony	119.5	120.4	120.0	120.
Argon	?	?	39.9?	40.
Arsenic	74.45	75.0	75.0	75.
Barium	136.4	137.40	137.43	137.4
Bismuth	206.5	208.1	208.0	208.5
Boron	10.9	11.0	10.95	11.
Bromine	79.34	79.95	79.955	79.96
Cadmium	111.55	112.4	112.3	112.
Caesium	131.9	132.9	132.9	133.
Calcium	39.8	40.1	40.1	40.
Carbon	11.9	12.0	12.001	12.00
Cerium	138.0	139.0	140.	140.
Chlorine	35.18	35.45	35.455	35.45
Chromium	51.7	52.1	52.14	52.1
Cobalt	58.55	59.00	59.00	59.
Columbium	93.0	93.7	94.	94.
Copper	63.1	63.6	63.60	63.6
Erbium	164.7	166.0	166.	166.
Fluorine	18.9	19.05	19.05	19.
Gadolinium	155.8	157.0	156. ?	....
Gallium	69.5	70.0	70.0	70.
Germanium	71.9	72.5	72.5	72.
Glucinum	9.0	9.1	9.1	9.1
Gold	195.7	197.2	197.3	197.2
Helium	?	?	4.0?	4.
Hydrogen	1.000	1.008	1.0075	1.01
Indium	113.1	114.0	114.	114.
Iodine	125.89	126.85	126.85	126.85
Iridium	191.7	193.1	193.0	193.
Iron	55.6	56.0	56.0	56.
Lanthanum	137.6	138.6	138.5	138.
Lead	205.36	206.92	206.92	206.9
Lithium	6.97	7.03	7.03	7.03
Magnesium	24.1	24.3	24.36	24.36
Manganese	54.6	55.0	55.02	55.
Mercury	198.50	200.0	200.0	200.3
Molybdenum	95.3	96.0	96.0	96.
Neodymium	142.5	143.6	143.6	144.
Nickel	58.25	58.70	58.70	58.7

| | Clarke. | | | |
	$H = I$.	$O = 16$.	Richards.	German.
Nitrogen	13.93	14.04	14.045	14.04
Osmium	189.6	191.0	190.8	191.
Oxygen	15.88	16.000	16.0000	16.00
Palladium	106.2	107.0	106.5	106.
Phosphorus	30.75	31.0	31.0	31.
Platinum	193.4	194.9	195.2	194.8
Potassium	38.82	39.11	39.140	39.15
Praseodymium	139.4	140.5	140.5	140.
Rhodium	102.2	103.0	103.0	103.
Rubidium	84.75	85.4	85.44	85.4
Ruthenium	100.9	101.7	101.7	101.7
Samarium	149.2	150.3	150.0	150.
Scandium	43.8	44.1	44.	44.1
Selenium	78.6	79.2	79.2	79.1
Silicon	28.2	28.4	28.4	28.4
Silver	107.11	107.92	107.930	107.93
Sodium	22.88	23.05	23.050	23.05
Strontium	86.95	87.60	87.68	87.6
Sulphur	31.83	32.07	32.065	32.06
Tantalum	181.5	182.8	183.	183.
Tellurium	126.5	127.5 ?	127.5 ?	127.
Terbium	158.8	160.	160.	....
Thallium	202.61	204.15	204.15	204.1
Thorium	230.8	232.6	233.	232.
Thulium	169.4	170.7	170.?	....
Tin	118.1	119.0	119.0	118.5
Titanium	47.8	48.15	48.17	48.1
Tungsten	182.6	184.	184.4	184.
Uranium	237.8	239.6	240.	239.5
Vanadium	51.0	51.4	51.4	51.2
Ytterbium	171.9	173.2	173.	173.
Yttrium	88.3	89.0	89.0	89.
Zinc	64.9	65.4	65.40	65.4
Zirconium	89.7	90.4	90.5	90.6

PRELIMINARY COMMUNICATION ON THE CHEMISTRY OF MUCIN.[1]

By P. A. Levene.

THE proteids may be divided into two main groups : First, simple proteids, second, combined proteids. Of the latter the most common are the nucleo-compounds and the mu-

[1] Read before the New York Section of the American Chemical Society, November 10, 1899.

cins. The mucins at present are considered to be compounds of proteids with carbohydrates. This assumption is based on the fact that all the mucins and allied compounds yield, on prolonged treatment with dilute mineral acids, substances reducing Fehling's solution in the same manner as glucose. The true nature of these substances was, however, unknown to the first workers on mucin.

The first successful attempt to obtain a pure carbohydrate was made in Hoppe-Seyler's laboratory. Landwehr stated that he obtained from various mucins a substance very similar in its properties to gum and named it " animal gum." He did not, however, view mucin as consisting of proteid and animal gum, molecularly combined. In his opinion mucins were only a mixture of the two substances. His views on this latter point were subsequently retracted by the author. After Landwehr almost every investigator working on this subject sought for the same "animal gum," and many claimed to have obtained it. Hammarsten succeeded but once in obtaining from mucin a nitrogen-free substance, which, on heating with mineral acids, was capable of reducing an alkaline copper solution. Loebish asserted that by following the conditions indicated by Landwehr he obtained the same "animal gum" from the mucin of fibrous tissue.

A new series of investigations on the entire question of " animal gum" was very recently undertaken by Folin in Hammarsten's laboratory. The latter doubting for certain reasons the correctness of Landwehr's statements, followed as closely as possible all the conditions prescribed by Landwehr, the substances thus obtained never being free from proteid material. Instead of "animal gum" he obtained a " mucinalbumose." Most of the other workers investigated only the composition of the various mucins as such, or the "carbohydrates" resulting from heating the mucins with dilute mineral acids.

There is, however, one property of all the mucins, to which sufficient attention has not been directed. The mucins possess very marked acid properties, more distinct than any simple proteid, and, in fact, more than any carbohydrate, which display no acid character whatever. In explanation of the acid properties two assumptions may be made : First, the substance reducing copper (formed on heating with mineral acids), may be an acid

derivative of some carbohydrate, and secondly, there may be some acid besides the proteid and carbohydrate in the mucin molecule. Loebisch had already noticed that his "animal gum" would decompose carbohydrates, and Hammarsten stated that he could obtain a substance with acid properties from mucins.

The object of this work was to make a thorough study of the acid part of the mucin molecule. My first experiments were made on tendo-mucin obtained according to the method of Chittenden and Gies. The pure mucin was treated for twenty-four to forty-eight hours with a 2 per cent. sodium hydroxide solution and from this solution a substance with acid properties was obtained, by a very simple method, which will be described when the work is completed.

On more detailed examination the substance proved to be nitrogenous. It did not, however, give the biuret reaction, and consequently was free from proteids. On boiling with dilute hydrochloric acid the substance reduced Fehling's solution. The solution of the substance on addition of hydrochloric acid and barium chloride remained perfectly clear, but on boiling yielded a white precipitate. All these properties are peculiar to chrondroitin-sulphuric acid. Hence it was natural to assume some relationship between the two substances. Two grams of the substance were heated on a water-bath in 100 cc. of 3 per cent. nitric acid until the solution gave no precipitate with alcohol (this consumed about twenty hours). Several volumes of alcohol and ether were then added to this solution. This yielded only an opalescence ; upon addition of a few drops of sodium chloride solution, however, a fine white precipitate formed, which gave the barium test for chrondrosin.

The substance gave a precipitate with a solution of Witte's peptone only on addition of acetic acid as long as there was still some of the sodium salt present. When the acid was free from sodium salts, it gave on standing with a neutral albumose solution a flocculent slimy precipitate, resembling genuine mucin. Copper, sodium, and barium salts of the substance were also obtained.

ANALYSIS OF THE COPPER SALT.

0.358 gram of the substance was decomposed with hydrochloric acid ; the copper was precipitated with hydrogen sulphide and

weighed as CuO ; 0.0446 gram CuO, or 9.97 per cent. metallic copper was obtained.

Schmiedeberg found the percentage of copper varying between 9.04 and 10.20 per cent. In all these properties, as well as the copper content, this substance resembles chrondroitinsulphuric acid.

The next question was whether this ethereal or compound sulphuric acid was only a contamination of the mucin, or constituted an integral part of it. Some of the mucin prepared as above was dissolved in 1 per cent. sodium carbonate, and immediately treated as before for the isolation of the acid ; only traces were, however, obtained. The residue was washed and redissolved and again treated in like manner ; here also only traces were detected. The residue was then thoroughly washed with distilled water until the substance was entirely washed out. The residue was left for twenty-four hours in 200 cc. of 2 per cent. solution of sodium hydroxide. It was then treated as above for the isolation of the substance. The yield was a very good one. I also observed that the acid can be split off from mucin on digesting the latter on the water-bath with addition of a few drops of hydrochloric acid. On digestion with pepsin-hydrochloric acid the mucin also yielded the same acid even after twenty-four hours of digestion. After three weeks of digestion part of the mucin, however, remained undissolved. The investigation into the nature of the residue, as well as of the proteoses thus formed, has so far not been completed.

The next question was whether only the tendo-mucin is a compound of an ethereal sulphuric acid, or whether all the mucins and mucoids have the same composition. The investigation before us thus far embraces only the submaxillary mucin and the substance of a mucoid carcinoma. The submaxillary mucin was obtained by the following method : Freshly removed glands were placed in ether immediately after the death of the animal, and then brought to the laboratory. There they were minced in a chopping machine and allowed to macerate with distilled water for twenty-four hours (large quantities of chloroform being added to keep the tissue from decomposing). The extract was then strained through gauze, well shaken with ether in separatory funnels, and left in the latter for twenty-four hours.

This process caused all the tissue particles and the fat to collect on the surface, the lower layer remaining perfectly clear. It was then filtered and treated for mucin according to the method of Hammarsten. The substance was redissolved and reprecipitated twice. This mucin was treated in the same way as the tendo-mucin for the ethereal sulphuric acid. But instead of the latter a substance was obtained very similar to that obtained by Folin in Hammarsten's laboratory, and which he called mucinal-bumose.

After several futile attempts to obtain the acid free from proteids I finally obtained positive results by the following method : The mucin was digested for one hour in a Koch sterilizer with 0.1 per cent. hydrochloric acid solution. The solution, being then neutralized with sodium hydroxide, was treated with large quantities of alcohol. The precipitates thus formed were treated with 5 per cent. sodium hydroxide and allowed to stand over night. This solution was treated in two different ways, each yielding positive results : (1) The solution was treated with Brucke's reagent and hydrochloric acid. The filtrate did not give any precipitate on addition of alcohol and ether. If, however, a sufficient quantity of sodium hydroxide was added previously to the alcohol to render the solution slightly alkaline, a yellowish precipitate was formed very similar to that of the sodium salt of the ethereal sulphuric acid. The precipitate was redissolved in dilute sodium hydroxide solution, filtered and reprecipitated with alcohol. The substance thus obtained precipitated an acid solution of albumose, reduced Fehling's solution on boiling with hydrochloric acid, and on addition of hydrochloric acid and barium chloride gave a precipitate only upon heating. It was nitrogenous and did not give the biuret reaction. There was not enough of the substance to attempt the chrondrosin test.

In another experiment phosphotungstic acid was used instead of Brucke's reagent. The result was the same.

From this may be concluded that the submaxillary mucin contains in its molecule a substance which is either chondroitin-sulphuric acid or closely related to it. The investigation of a mucoid carcinoma by the same method as the submaxillary mucin revealed the presence of a similar substance. The study

of ovomucoid, mucoid of the thyroid gland and of a mucoid tumor is now in progress.

I was prompted to make the present communication by the fact that about ten days ago an article appeared in Hoppe-Seyler's *Zeitschrift*. The author analyzed an ovarial mucoid and found a substance similar to chondroitinsulphuric acid. His findings on the latter mucoid coincide with mine on several mucins and justify the conclusions I was ready to draw from my work, that mucins are not simple compounds of proteids and carbohydrates, but are proteid derivatives of an ethereal sulphuric acid.

I consider it premature at this moment to state positively the nature of this combination.

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THE DETERMINATION OF GLYCOGEN AND RELATIVE QUANTITIES OF GLYCOGEN IN DIFFERENT PARTS OF THE FLESH OF A HORSE.

BY J. K. HAYWOOD.

A GREAT many methods have been proposed for the estimation of glycogen,[1] but on trying them I found that nearly all were open to some serious objection, which rendered their employment either entirely out of the question or the results obtained very doubtful. I have, therefore, worked out a method which, although not new in principle, is new in many of the details which go to making up a fairly accurate and speedy procedure. But first I will speak of some of my preliminary experiments to show future workers in this field, at least, what *not to do*.

[1] Wiley's "Principles and Practice of Agricultural Analysis", 3, 554.

Having seen in a paper by Von Wittich[1] that glycogen might be determined by digesting the sample of meat on the steam-bath for two or three hours, with water containing a few drops of sulphuric acid, filtering, neutralizing, filtering again, determining the reducing sugar in the filtrate by Fehling solution, and from that figure calculating the glycogen, I thought I would try this, as it seemed the easiest way. I added, however, more than a few drops of sulphuric acid,—in fact, made a 3 per cent. solution; for it is well known that glycogen is more resistant to the action of acids than starch, and a few drops of sulphuric acid would not convert starch in this time. I also continued the digestion for six hours. I encountered a difficulty at once; i. e., the mixture would not filter after digestion, except very slowly,—so slowly that a practical use of the method was impossible. I therefore neutralized immediately after digestion, made to a volume, and filtered off an aliquot portion, which still took a long enough time, but was much shorter than filtering the whole. Using a dried, ether-extracted liver, I obtained results of 1.27 and 1.29 per cent. glycogen, which looked encouraging from the closeness of the duplicates. The Fehling solution filtrate, however, looked dirty, and the copper suboxide precipitated was not red, but a dirty green, such as no chemist likes to see.

I therefore carried through a sample of the liver, using the above method, except that at the end the solution was clarified with lead subacetate, the excess of lead removed by sodium sulphate, and the dextrose determined in the filtrate. In this way a clear Fehling filtrate was obtained, but the results did not at all compare either with each other or with those (1.29 and 1.27) mentioned above. In one case I obtained a result of 0.87 per cent. glycogen, and in a duplicate 0.00 per cent. glycogen.

Thinking from the work of Külz and Bornträger[2] that hydrochloric acid might be a better agent to convert the glycogen to dextrose, I next boiled some of the liver for three hours with 200 cc. of water and 20 cc. of hydrochloric acid (sp. gr. 1.125), neutralized with sodium carbonate, and filtered just as in the determination of starch. The result on a non-clarified portion was 4.72 per cent. glycogen, and on a portion clarified by lead

1 Central-Blatt. f. d. med. Wissenschaft, 13, 292 (1875).
2 Archiv. f. d. ges. Physiologie, 24, 28.

subacetate, and the excess of lead removed by sodium sulphate, the result was 1.25 per cent. glycogen. I again determined the glycogen as above, except that the solution at the end was clarified with neutral lead acetate, and results of only 0.03 and 0.04 per cent. glycogen were obtained.

I next added 1 per cent. of starch to a sample of meat which gave no glycogen by the above method, and 1 per cent. of glycogen to another portion of the same meat. The samples thus prepared were treated just as in the determination of starch, and at the end clarified with neutral lead acetate, and the excess of lead removed. Proceeding in this way I could only recover 0.08 per cent. starch and 0.00 per cent. glycogen.

With results thus varying in the case of a sample of liver from 0.00 per cent. to 4.72 per cent., and results of 0.00 per cent. and 0.08 per cent., where 1 per cent. of glycogen and 1 per cent. of starch respectively had been added, it appeared that the method was absolutely worthless ; so it was abandoned.

It may seem strange, at first sight, that no better results than the above could be obtained following after Külz & Bornträger[1] who had worked out a method based on the inversion of glycogen to dextrose and the determination of the latter by Fehling solution ; but this apparent contradiction will disappear when I call attention to the fact that Külz only worked on *pure* glycogen, and in no case mixed his glycogen with meat and recovered it.

I did not make an attempt to estimate glycogen by means of the polariscope, as also given by Külz,[2] because Külz had worked with rather large quantities, so that if only 0.00 to 1.5 per cent. of glycogen were present the determination would be very uncertain, since if a workable quantity of the meat were used (say 50 to 60 grams), the reading on the sugar scale would be only a few tenths of a degree.

Estimating glycogen by the depth of its color with iodine, according to Goldstein,[3] was not employed, as it has been shown to be worthless by many subsequent investigators.

A qualitative test for glycogen by the test of Bräutigam and

[1] *Archiv. f. d. ges. Physiologie*, **24**, 28.
[2] *Ibid.*, **24**, 87 and **24**, 90.
[3] *Verhandlungen der physik-med. Gesell. in Würzburg*, **7**, 1.

Edelmann,[1] by means of iodine, was not employed, because subsequent investigators have been able to obtain the same test with other meats besides horse meat, notably on beef.

I therefore decided to try the method of Brücke,[2] which appeared to promise better results than any of the other gravimetric methods. Brücke digests the meat on the steam-bath with water, filters, precipitates the proteid matter in hydrochloric acid solution with the double iodide of potassium and mercury, again filters, precipitates the glycogen in the filtrate with alcohol, filters on a weighed filter, washes first with 60 per cent. alcohol, then with 95 per cent. alcohol, then with ether, dries at 115° C., and weighs. This method has been examined by many later investigators. Külz[3] found that an extraction of the meat with water was not sufficient, but that it was better to employ a weak solution of potassium hydroxide. Kratschmer[4] found that the hydrochloric acid of the Brücke reagent acted on the freshly precipitated glycogen ; also that it was best to first dry the glycogen at 80°–100° C., and then at 115°. I took all of these points into consideration when working out the method.

But first of all a serious difficulty was met with. It was found impossible to filter the meat digested with potassium hydroxide in a reasonable length of time, and nearly impossible to get off any fair-sized aliquot portion. Instead of filtering after the digestion with a weak solution of potassium hydroxide, the mixture was made immediately acid with hydrochloric acid, in the presence of the unattacked residue, Brücke's reagent added to precipitate proteid matter, the whole made to a volume, and an aliquot portion filtered off. In this way a very easily filterable mass was obtained. After an aliquot portion, say 250 cc. out of 500 cc., had been thus obtained, it was neutralized with a solution of potassium hydroxide (using a drop of phenolphthalein as indicator, and noting the amount of hydroxide employed) to get rid of the hydrochloric acid, which would, according to Kratschmer, act on the glycogen. When exact neutralization had been obtained, small flakes of some non-glycogen material would usually separate out. These were filtered

1 Ztschr. anal. Chem., 33, 98.
2 Central-Blatt f. d. med. Wissenschaft, 1871, 388.
3 Ztschr. für Biologie, 22, 161.
4 Archiv. f. d. ges. Physiologie, 24, 134.

off, a few drops of hydrochloric acid added to the filtrate, and twice the volume of 92 to 95 per cent. alcohol added. The precipitated glycogen was, at the end of a few hours, filtered off through a weighed filter, washed first with 60 per cent. alcohol, then with 95 per cent. alcohol, then with ether, dried at 80°-100° C., then at 115° C. and weighed again, the gain representing glycogen. In this way a result of 0.51 per cent. was obtained on a dry roast beef, and where 0.87 per cent. and 1.61 per cent. glycogen were added, 0.82 per cent. and 1.54 per cent. respectively were recovered. In each of the above determinations, however, something seemed to come down besides the glycogen, and on treating the filter with hot water this would mostly remain as a residue, and the glycogen be dissolved. It appeared from this, then, that a much better method than the one above was to weigh the filter and contents after drying, then dissolve out glycogen with water, dry and weigh again, and thus determine glycogen by the difference in weight. To test this I carried through a sample of roast beef, and on the water-free, fat-free sample by first method obtained a result of 0.3 per cent. glycogen ; by second, 0.17 per cent. glycogen ; on a liver I obtained 1.53, 1.56 per cent. by the first, and by second, 1.04, 1.10 per cent.; on a chicken I obtained 0.35 per cent. by the first, and by the second 0.26 per cent. It would therefore appear that all of the proteid matter was not precipitated by the double iodide of potassium and mercury, but that some which was nearly entirely insoluble in water came down with the glycogen and remained on the filter when the glycogen was dissolved.

From all of the above work I have settled upon the following method for determining glycogen. From 50 to 60 grams of meat, after having been run through a sausage grinder, is treated in an evaporating dish with 300 cc. of a 1 per cent. potassium hydroxide solution, and heated on the steam-bath for about six hours, water being added from time to time, so that the volume never becomes less than 150 cc. Finally the water is removed by evaporation until about 150 cc. remain. This is made slightly acid with hydrochloric acid (1–5), and hydrochloric acid and double iodide of potassium and mercury[1] added alternately until all pro-

[1] The double iodide of potassium and mercury is prepared by first precipitating a solution of mercuric chloride with potassium iodide, washing the precipitated mercuric iodide till free of chlorides, then saturating a 10 per cent. potassium iodide solution with the mercuric iodide at the boiling temperature

teid matter is precipitated. The hydrochloric acid is added
about 2 cc. at a time, and the double iodide of potassium and
mercury about 10 cc. at a time. Usually about 20-25 cc. acid
(1–5) and 70–100 cc. of the iodide solution are required. When
the proteid matter separates, and leaves a clear liquid layer
above, a small amount of this is carefully poured off and tested
for complete precipitation. If the precipitation is not complete
the liquid is returned, and the proteid precipitant added until
the clear liquid above the proteid matter gives no precipitate
with hydrochloric acid and the double iodide solution. Some-
times, not often, the proteid matter will not separate. In this
case follow Külz's method of nearly neutralizing with potassium
hydroxide and adding again hydrochloric acid, and the precipi-
tate will usually flocculate. The proteid matter being now pre-
cipitated as completely as possible, the whole is transferred to a
500 cc. flask, made to the mark with water, well shaken, and an
aliquot portion (say 250 cc.) filtered through a fluted filter. A
drop or two of phenol phthalein is now added, and the solution
titrated to exact neutrality with a concentrated solution of potas-
sium hydroxide, noting the amount used. If a slight amount of
flakey-looking matter separates at this point, the liquid is again
passed through a fluted filter, and such a volume taken as will
correspond to 2/5 of the original material, of course taking into
consideration the number of cubic centimeters of potassium
hydroxide used to neutralize the hydrochloric acid. Three or
four drops of concentrated hydrochloric acid are now added, and
twice the volume of from 93 to 95 per cent. alcohol. After stand-
ing two or three hours the precipitated glycogen is filtered off
through a paper filter, washed with 60 per cent. alcohol, then
with 95 per cent. alcohol, then with ether; dried at 80°–100° C.,
then at 115° C., and weighed in a weighing tube. The filter is
then extracted thoroughly with boiling water, dried again at
115° C., and again weighed in a weighing tube, the difference
in weight representing glycogen.

Proceeding in this way, I obtained on roast beef 0.17 per cent.
glycogen, calculated to the dry, fat-free basis ; where 0.87 per
cent. glycogen was added, 0.78 per cent. was recovered ; and
where 1.72 per cent. glycogen was added, 1.57 per cent. was

recovered. Close duplicates were also obtained by this method, as shown from the following work :

On a liver the results were 1.04 and 1.10 per cent. calculated to dry, fat-free basis.

On a chicken the results were 0.26 and 0.29 per cent. calculated to dry, fat-free basis.

On an ox tongue the results were 0.27 and 0.30 per cent. calculated to dry, fat-free basis.

On another ox tongue the results were 0.65 and 0.62 per cent. calculated to dry, fat-free basis.

Following will be found the analysis of three parts of three different horses, the glycogen of which was determined by the above method. First I will mention, however, that in addition to the direct determination of glycogen I also estimated the reducing sugars in a water extract of each sample of meat, as suggested by Niebel[1] to find the amount of glycogen that had been converted to dextrose. This was done by boiling the meat three separate times with 500 cc. portions of water, pouring off the water each time, evaporating to a small volume, clarifying with neutral lead acetate, removing excess of lead with sodium carbonate, making to a volume, filtering off an aliquot portion, and determining the dextrose in the filtrate by Allihn's method.

No. of sample.	Part of horse.	Water. Per cent.	Fat. Per cent.	Glycogen. Per cent.	Glycogen corresponding to dextrose. Per cent.	Glycogen in each of the preceding columns calculated to fat-free, water-free basis. Per cent.	
1	chuck	70.57	9.01	0.30	0.00	1.47	0.00
2	chuck	74.30	4.63	0.48	0.00	2.28	0.00
3	chuck	77.22	5.84	0.86	0.00	5.08	0.00
4	rib	66.12	12.51	0.61	0.00	2.85	0.00
5	rib	72.87	4.54	0.54	0.00	2.39	0.00
6	rib	76.31	1.24	0.79	0.00	3.52	0.00
7	flank	57.93	25.01	0.42	0.00	2.46	0.00
8	flank	71.79	7.66	0.33	0.00	1.61	0.00
9	flank	76.39	1.16	0.53	0.00	2.36	0.00

In four of the above samples a determination was made of the amount of nitrogen in the glycogen dissolved from the filter, to

[1] *Ztschr. f. Fleisch. u. Milch. Hygiene*, **1**, 185, 210, and **5**, 86, 130.

see how much, if any, proteid matter had not been removed, but still contaminated the glycogen.   In four more of the above samples a determination was made of the amount of ash in the glycogen to see if a correction was necessary.   The results are given below.

No. of sample.	Amount of original beef used.	Amount of beef used in actual determination, being 2/5 of original.	Amount of glycogen found.	Amount of proteid matter $6.25 \times N$.	Amount of ash.
	Grams.	Grams.	Grams.	Grams.	Grams.
1	60	24	0.0717	0.0009	....
2	60	24	0.1148	....	0.0048
3	60	24	0.2070	....	0.0065
4	60	24	0.1467	0.0018	....
5	60	24	0.1304	0.0017	....
6	60	24	0.1898	0.0024	....
7	60	24	0.0999	....	0.0030
9	60	24	0.1282	....	0.0025

It will thus be seen that only a small percentage of the glycogen consists of proteid matter and ash, and when these two are added together, and calculated back as per cent. of the original substance, the figure for glycogen will only be altered by about 0.02 per cent.

In several other determinations of glycogen, the glycogen which was dissolved from the filter was evaporated to a small volume and tested with Brücke reagent and with bromine, to see if any proteid matter was precipitated.   In no case did any come down.

From this work it will be seen that the glycogen obtained is quite pure, only a small portion consisting of ash and proteid matter.   The small plus error caused by these substances, in all probability, about balances the negative error caused by the action of hydrochloric acid on the glycogen during the precipitation of proteid matter.

While the above method is, I think, much more accurate than the original Brücke method, it does not possess the accuracy of a chlorine or sulphuric acid determination, but this is not necessary, since the end of the work is not to know the amount of glycogen to 0.01 per cent., but to distinguish horse meat from other meats by its high content of glycogen.

Appended will be found analyses of several parts of a single horse. These are not given to show anything about the accuracy of the method, but to increase the data relating to the amount of glycogen in different cuts of horse meat. The horse was one which had been killed in an accident, three days before the analysis was made.

No. of sample.	Part of horse.	Water.	Fat.	Glycogen.	Glycogen corresponding to dextrose.	Glycogen in each of the preceding columns, calculated to fat-free, water-free basis.	
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
1	Second cut of round··	74.36	3.27	0.49	0.00	2.19	0.00
2	First cut of round····	73.77	3.23	0.27	0.05	1.17	0.22
3	Shoulder clod········	73.54	5.27	0.58	0.05	2.73	0.23
4	Cross ribs···········	73.86	6.30	0.32	0.04	1.62	0.20
5	Chuck···············	68.00	15.39	0.34	0.00	2.05	0.00
6	Plate ··············	52.16	33.66	0.41	0.00	2.89	0.00
7	Brisket ·············	66.70	12.16	0.46	0.006	2.17	0.03

I would like to express my thanks to Dr. W. D. Bigelow, of this Division, for putting at my disposal a very complete bibliography of glycogen. Since his work will shortly appear in print, I will not attempt to go into the literature of the subject.

THE ELECTROLYTIC DEPOSITION OF BRASS.

BY J. LIVINGSTON R. MORGAN.

BRASS plating by electrolysis was discovered in 1841, and the original process, with a few modifications, is still in use at the present time. The formulas for the preparation of the bath are entirely empirical, the subject, so far as I know, having never been treated from the theoretical standpoint. The purpose of this paper is to consider the reaction by the light of our present knowledge of electrochemistry, and to present the theory of the process which results.

When a metal with a high electrolytic solution pressure (Zn) is placed in an acid solution and connected by a wire to a plate of platinum, immersed in the same liquid, hydrogen gas is

given off, at the platinum side, in the form of bubbles. The chemical reaction is

$$M + \overset{+}{H} + \overset{-}{A} = \overset{+}{M} + \overset{-}{A} + H \, \text{gas},$$
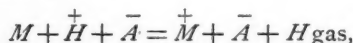
where M represents a monovalent metal, and HA a monobasic acid, which is dissociated into the ions $\overset{+}{H}$ and $\overset{-}{A}$. The process consists, essentially, in, the formation of metallic ions, which force ions of hydrogen out of the solution. A certain difference of potential results from this reaction which may be calculated by aid of the formula

$$\pi = \frac{0.0002}{n} \, T \log. \frac{P}{p} - 0.0002 \, T \log. \frac{P_1}{p_1} \, \text{volts},$$

where n is the valence of the metal, P its electrolytic solution pressure, and p the osmotic counter pressure of the metallic ions in solution, while P, and p, are the corresponding figures for hydrogen. The end of such a reaction will be reached, of course, when the solution is saturated with ions of the metal; $i.\,e.$, when all ions of hydrogen have disappeared.

When a metal possessing a low electrolytic solution pressure (Cu) is placed in acid, no hydrogen gas is given off, and ions of this metal in a solution would precipitate in the metallic form upon the plate.

When the metal plate in the above arrangement is used as the anode of a decomposition cell the general action of a metal with a high electrolytic solution pressure is the same, only intensified. With a metal of low electrolytic solution pressure the action is reversed so that if the electromotive force is made sufficiently high the metal acts as one of the former class and separates hydrogen from the acid. The value of the term P then can always be increased by an external electromotive force. Thus by reversing a Daniell cell and sending a current from the copper to the zinc, through the liquid, copper is dissolved and zinc precipitated. If a solution of a copper salt is electrolyzed with a copper anode, the value of P is increased until it exceeds the value p; $i.\,e.$, the osmotic counter pressure of the copper ions. At the cathode the copper ions accumulate, and are forced out of a solution upon the plate. With copper this would naturally take

place even without a great accumulation of ions, but with a metal of high electrolytic solution pressure the ions would separate only when the term p is made greater than P. The work necessary for plating with a metal of high electrolytic solution pressure is thus seen to be done at the cathode, for there P must be exceeded by p, while for one with a low electrolytic solution pressure it is done at the anode for there it is necessary for P to exceed p in value. In other words metals like zinc, in simple solutions, need the current to separate them from the solution, while those like copper need it to cause the anode to dissolve. If the decomposing electromotive force is great enough, hydrogen will also be separated at the cathode, for ions of hydrogen will accumulate then and be evolved as gas when the electromotive force causes p_1 to exceed P_1 in value. With a small electromotive force, however, this will not take place so that for our purposes we may leave it out of consideration entirely.

If an alloy, made up of two metals one of which has a very high electrolytic solution pressure, while the other has a very low one, is placed in acid the constituent with the high pressure will dissolve, separating hydrogen gas upon a platinum plate, while the other will be unaffected. The end of the reaction will be reached when the acid is saturated with the ions of the one metal or if there is an excess of acid, when the one metal is entirely dissolved. Using such an alloy as the anode of a decomposition cell, both constituents will go into solution. The amounts dissolved will be proportional to the values of the electrolytic solution pressure. If the electrolyte in the cell contains ions of each constituent, then at any one decomposing electromotive force the amounts dissolved will be proportional to the electrolytic solution pressures divided by the osmotic counter pressures of the metallic ions. If the alloy contains 50 per cent. of each constituent it will be necessary for its solution in unchanged ratio, that $\frac{P}{p} = \frac{P'}{p'}$, where P and P' are the electrolytic solution pressures of the two metals and p and p' the osmotic pressures of their ions. In other words it is necessary that the ionic concentration of the metals be proportional to the electrolytic solution pressures. This relation is shown most plainly by the following diagram :

$$\left. \begin{matrix} \text{Cu} \\ \text{Zn} \end{matrix} \right\} 50 \text{ per cent.} \quad \left|\left| \begin{matrix} \rightarrow P_{\text{Cu}} = 4.8 \times 10^{-20} \text{At.} \\ \leftarrow p_{\text{Cu}} = 4.8 \times 10^{-20} \text{At.} \\ \leftarrow p_{\text{Zn}} = 9.9 \times 10^{+18} \text{At.} \\ \rightarrow P_{\text{Zn}} = 9.9 \times 10^{+18} \text{At.} \end{matrix} \right.\right.$$

The two opposing pressures, osmotic and electrolytic solution, are thus equalized for each of the two metals ; hence an electro-motive force applied to the alloy as anode will cause equal amounts of copper and zinc to be dissolved. Such a mixture would be made if a saturated solution of a zinc salt were in contact with a plate of the 50 per cent. alloy, and the alloy, when made the anode, would dissolve evenly. It is necessary now, however, to consider the cathode upon which the metal will be precipitated. Here we will not get, at any current density, the alloy we expect so that the relation between the zinc and copper ions in the solution will change, and consequently the two constituents will then be dissolved from the anode in another ratio. *For the deposition of any alloy, then, we see that it is necessary that the following conditions be fulfilled: 1. That the solution have such an ionic concentration of the two metals that the correct amount of each constituent dissolves from the anode ; i. e., that the alloy dissolves as such. 2. That the correct alloy separates at the cathode, so that the composition of the liquid is not altered in such a way that the first condition is unfulfilled.* With alloys of copper and zinc we see that, for simple salt solutions, the first condition can be fulfilled, but the second can not.

A solution from which brass may be deposited and which will retain this power, by dissolving the correct proportions of copper and zinc from the anode, must have the following properties, which are self-evident from what has already been said: *1. It must contain ions of zinc and copper in such a proportion that 30 per cent. of zinc, and 70 per cent. of copper will be dissolved from the anode ; i.e.,* $\dfrac{P}{p} : \dfrac{P'}{p'} : : 30 : 70$. *2. It must contain complex ions of zinc and copper, from which these metals may be separated.* These are necessary, for we have seen that simple metallic ions cause changes in the composition of the solution and thus vary the composition of the alloy dissolved. There is also less work needed to separate metals from complex ions than from simple ones. *3. For economy, the maximum concentration of copper*

ions should be as small as possible in order that copper may be separated easily from the anode.

All these conditions are fulfilled by a solution of the mixed salts of copper and zinc in potassium cyanide solution. We have first an extremely small concentration of zinc and copper ions. The absolute value of the concentration of copper ions can be appreciated from the consideration of the following experiment : When a solution of potassium cyanide is poured upon the copper side of a Daniell cell, the poles are reversed ; *i. e.*, copper becomes the negative pole. In order to do this, it is necessary that

$$\frac{P}{p} \text{ (ZnSO}_4) < \frac{P'}{p'} \text{ (CuSO}_4 \text{ in KCN);}$$

i. e., that the value of p becomes so small that $P' (= 4.8 \times 10^{-20})$ exceeds it and copper goes into solution. We have the complex ions $\overline{Z}n(\overline{C}N)_4$ and $\overline{C}u(\overline{C}N)_4$, from which zinc and copper may be deposited in varying proportions according to the current density, for zinc needs a greater current density than copper. In other words from our theoretical knowledge we can predict that such a solution would serve our purpose.

It would seem necessary, next, to find just what proportion of zinc and copper salt should be present in the cyanide solution, to give the correct ratio of ions. This, however, is not necessary, as is shown by the following consideration, for this ratio adjusts itself automatically during the reaction. In practice, at times, a bath is made up as follows: A solution of potassium cyanide is electrolyzed, at the correct density to deposit brass, for several hours with brass electrodes, the liquid being drawn off and used as the bath. From the brass anode ions of zinc and copper ions are given off into the solution forming the salts K_2ZnCN_4 and K_2CuCN_4. These salts dissociate, to a very large extent, into $\overset{+}{2K}$ and $\overline{M}CN_4$, where M represents either copper or zinc. There is also a further dissociation, to a very slight degree, into $\overset{+}{2K}$, $\overset{++}{M}$ and $4\overline{C}N$. The zinc, on account of its high electrolytic solution pressure, will dissolve to a greater extent than the copper, so that there will be more ions of $\overline{Z}n\overline{C}N_4$ than of $\overline{C}u\overline{C}N_4$. Only 30 parts of zinc, however, at this current density can separate to

every 70 parts of copper so that there is also a concentration of $\overline{Zn}\overline{CN}_4$ ions on the cathode side; this takes place after hydrogen has been given off for a time. The equilibrium in the solution is fixed by certain equations. By these only a certain amount of free zinc ions can exist in the solution, all over this amount being transformed into $\overline{Zn}\overline{CN}_4$, and of this latter a relatively small portion only can separate at the cathode. For this reason when the solution becomes saturated with $\overline{Zn}\overline{CN}_4$ ions, it exerts the same counter pressure with its free zinc ions as it would if the solution were saturated with zinc ions, since any more zinc ions would supersaturate the solution. For this reason zinc can only dissolve to the same amount in which it separates.

The copper ions in the solution are so few that, as before observed, the metal acts as though it possessed a high electrolytic solution pressure. There is a larger number of $\overline{Cu}\overline{CN}_4$ ions and since these break up and separate copper to a greater extent than those of $\overline{Zn}\overline{CN}_4$ separate zinc, and since the solution never becomes saturated with them, the terms $\dfrac{P}{p}$ and $\dfrac{P'}{p'}$ become of the same order, and are related as 30 : 70. It is thus seen that the regulation of the relative concentration of zinc and copper dissolved is automatic and depends upon the current density which regulates the ratio deposited. In few words we may sum up the behavior as follows: The solution is saturated with zinc, since no more can exist either as Zn or as $\overline{Zn}\overline{CN}_4$, except as Zn from $\overline{Zn}\overline{CN}_4$ separates. The relation $\dfrac{P'}{p'}$ is increased by the exceedingly small value of p' so that ions of copper can form, but as they form they separate on the other side, removing the saturated condition with respect to zinc, so that the correct relative amount of this also can separate and dissolve, etc.

Another method consists in dissolving equal weights of copper and zinc salts in a solution of potassium cyanide. The action, of course, is exactly similar to that given above for potassium cyanide solution alone, so that it will not be necessary for us to consider it.

It is thus possible from purely theoretical knowledge, and a few appropriate simple experiments to find just what solutions must be used for baths for the deposition of any alloy. The contrast between this method and the old empirical one of trying all combinations until a lucky hit is made, the true reasons for which are unknown, is striking, but it is just what is being experienced to-day in all branches of chemistry by the application of theory to practice. The other ingredients which are used in the baths are to produce a fine smooth coating and have nothing to do with the theory of the method. Of course there are other solutions which behave just as the double cyanides do, but as the theory is the same, the only idea of a change would be for economy and that is a question for the technical side of the subject. Such another solution which is used is made by dissolving zinc and copper salts in an excess of ammonia. Here we have just as before Zn and Cu ions, and also complex ones which behave just as $\overline{Cu}\overline{CN}_4$ and $\overline{Zn}\overline{CN}_4$.

Another liquid which causes copper to act as a metal of high electrolytic solution pressure is a solution of potassium sulphide.

THE DETERMINATION OF SULPHUR IN BITUMENS.

By A. C. Langmuir.

IN the September number of this Journal, S. F. and H. E. Peckham criticize a paper by E. H. Hodgson which appeared in November, 1898, and describe, in some detail, their own method slightly modified.

The authors claim for their method that it is "simple, reasonably rapid and accurate" and state that it is "susceptible of great accuracy, if *conducted with care*. It requires great care from the beginning to the end. Mr. Hodgson's results do not indicate great care,—they are not sufficiently concordant."

It is but fair to Mr. Hodgson to call attention to certain features in Messrs. Peckham's method which cannot inspire chemists with confidence and which may possibly indicate that the authors themselves have not bestowed on their method the great care which they miss in Mr. Hodgson's work.

A brief review of the method is necessary : Approximately

0.5 gram of the bitumen is fused with 30 grams of a mixture of equal parts of sodium carbonate and potassium nitrate in a platinum crucible. The crucible contents are dissolved in water, hydrochloric acid is added, and the silica is separated by evaporation on the water-bath and dehydration. After taking up with hydrochloric acid and water the silica is filtered and the filtrate is rendered alkaline with ammonia to precipitate iron and alumina. The excess of ammonia is removed by boiling, and the iron and aluminum are filtered off. The lime is removed by ammonium oxalate and in the filtrate from the latter, now free from silica, alumina, iron and lime, the sulphuric acid is precipitated by the usual method. The convenience of estimating the mineral constituents in the same solution with the sulphuric acid is noted. In our opinion, what is gained in convenience, if any, by this method, is lost in accuracy.

In some bitumens the amount of sulphur is very low. In others the proportion of mineral matter is so high that very considerable amounts of iron, alumina, or lime may be met in the course of the analysis.

If the above method is to be generally applied the following objections should first be answered:

In the course of the fusion with alkaline carbonate and nitrate there is danger of the absorption of sulphuric acid produced by the burning gas. Any error from this cause would be especially noticed in the analysis of bitumens low in sulphur. An alcohol lamp should be used or the crucible should rest in a hole cut in asbestos board to protect the fusion from the access of the products of combustion.

Messrs. Peckham have not given us details sufficient to enable us to decide whether they have made use of these necessary precautions. Several chemists have called attention to this danger.[1]

In the slow evaporation of the fusion on the water-bath there is again a possible source of error in the absorption of sulphur, if, as is often the case, the bath is heated by gas.

Hillebrand[2] finds that the sulphur introduced in this way in the analysis of silicate rocks is frequently as much as the entire sulphur present. The writer's own experience has confirmed

[1] Price : *J. Chem. Soc.*, London, **2**, 51; Fresenius: *Ztschr. anal. Chem.*, **16**, 339; Lunge : *J. prakt. Chem.*, **40**, 239

[2] Bull. U. S. Geol. Survey, **148**, 1897.

this statement entirely and rather than dehydrate for silica we have precipitated the sulphuric acid directly in the acidulated aqueous solution of the fusion. We have never found any silica in the barium sulphate so obtained, but if its presence is feared it may be readily removed with a little hydrofluoric and sulphuric acids.

How considerable the contamination of the evaporating solution may be is plain from the experiment of E. von Meyer[1] who found, after evaporating 2 liters of distilled water down to 50 cc. during six hours on the water-bath, the equivalent of 0.0426 gram barium sulphate present.

A third objection and the most serious of all is against the separation of iron and alumina by boiling out the excess of ammonia. It is well known that iron can only be precipitated free from sulphur in a solution containing the latter by adding a distinct excess of ammonia to the moderately warm solution, heating a few minutes on the water-bath and filtering immediately. Only in this way can the formation of insoluble basic sulphates be prevented. Boiling the solution is, of all things, to be avoided. Lunge[2] states that correct results can only be obtained by adhering strictly to this procedure and that deviations lead to serious errors.

The check analyses made by the authors do not controvert the criticisms just made as the asphalt analyzed was said to be very pure and was presumably free from mineral matter.

Finally, in view of the recognized tendency of barium sulphate to drag down with it other mineral constituents of the solution and barium salts of other acids present, what must be said of precipitating sulphuric acid in the presence of ammonium oxalate and the alkaline chlorides from 30 grams of mixed carbonate and nitrate?

Our preference is given to Eschka's method following the details as described by Heath.[3] The Eschka method is admittedly the best for the determination of sulphur in bituminous coals. The problem here is a very similar one. In addition to its convenience and rapidity the Eschka method has the

[1] *J. prakt. Chem.*, **42**, 267; see also Gunning : *Ztschr. anal. Chem.*, **7**, 480; Alex : *Ibid.*, **10**, 246; Wagner : *Ibid.*, **20**, 323; Lieben : *Ibid.*, **32**, 214; Privozink : *Ber. d. chem. Ges.*, **25**, 2200.

[2] *Chem. News*, **71**, 132; *J. prakt. Chem.*, **40**, 239.

[3] This Journal, **20**, 630.

advantage of leaving the iron, lime, and alumina insoluble at the start and only a small quantity of alkali is introduced into the analysis.

As for the mineral constituents they are better determined on a separate portion. Their accurate determination is made all the more difficult by the presence of an excessive amount of alkali metals as in Peckham's method.

Our practice has been to heat the asphalt at a low temperature in a platinum dish, slowly driving off the volatile constituents in such a way that the asphalt does not burn. At the end the temperature may be raised and the remaining organic matter burned without danger of loss.

The ash is extracted with hydrochloric acid and any insoluble residue fused with a small amount of the mixed carbonates. The solution of the fusion in hydrochloric acid is added to the other and the analysis proceeded with as usual. In this way the quantity of alkaline salts is reduced to a minimum.

Time is actually lost by determining the metals and sulphur in one portion as the determination of the latter must wait until the metals have been separated.

In all but two of the asphalt analyses of Dr. Day, as quoted by Messrs. Peckham, the decimal point is misplaced, making the per cent. sulphur far less than it should be.

LABORATORY OF RICKETTS AND BANKS, NEW YORK.

THE DETERMINATION OF NICKEL IN NICKEL ORES.

BY A. C. LANGMUIR.

GEORGE WILLIAM SARGENT'S paper on the "Determination of Nickel in Nickel-Steel" in the October number of this Journal, prompts me to publish a somewhat similar method for the determination of nickel in its ores, which has been in use in this laboratory for several months with excellent results. It is particularly advantageous in all cases in which a relatively small quantity of nickel is to be separated from a large amount of iron and surpasses all other methods such as the basic acetate, basic carbonate, or ammonia separations.

One gram of the ore is covered in a No. 2 Griffin's beaker

with 15 cc. concentrated nitric acid.   One or two cc. of liquid
bromine is added and the contents are gently heated until the
bromine is expelled.   The solution is then boiled down almost
to dryness.   Bromine in combination with nitric acid effects so
thorough an oxidation that no sulphur bead can form.   This
reaction may also be applied in the analysis of copper mattes,
where it is often necessary to filter off the sulphur bead which
usually forms after the treatment with nitric acid and to roast it
to recover the small amount of undecomposed sulphide which it
invariably contains.   The addition of bromine renders this extra
operation entirely unnecessary.

After expelling the excess of nitric acid, about 50 cc. of con-
centrated hydrochloric acid are to be added and the solution
slowly boiled down to 5 cc.   The nitric acid is expelled and any
residue carrying nickel and insoluble in nitric acid is brought
into solution—at least in the ores handled by us.

Dilute to 250 cc. with hot water and pass hydrogen sulphide
to remove copper, etc.   Filter and boil the filtrate to expel
hydrogen sulphide.   Oxidize the ferrous iron by adding nitric
acid to the boiling solution, drop by drop, carefully avoiding any
excess.   Cool slightly and add ammonia until distinctly alkaline.
Filter and wash twice with hot water, catching the filtrate which
will contain the bulk of the nickel in a large casserole and boil
it down while the remaining operations are being performed.

Dissolve the ferric hydrate which carries a considerable
amount of nickel in warm dilute hydrochloric acid.   Wash into
a casserole and boil down rapidly until pasty.   Add about 10
cc. of hydrochloric acid (1.10 sp. gr.), warm slightly, rinse into
a 250 cc. separating funnel with acid of the same strength,
keeping the volume down to 50 cc., if possible, and cool
thoroughly.   Add now 40 cc. of C. P. ether and agitate
vigorously at least five minutes.   Invert the funnel occasionally
and open the stop-cock cautiously to lower the pressure.   The
ferric chloride gradually dissolves in the ether leaving the
nickel, aluminum, and any cobalt or manganese in the aqueous
solution as chlorides.

The first solution obtained by boiling down the nitric acid
residue with 50 cc. of hydrochloric acid cannot be profitably
treated by the ether separation.   On account of the sulphuric

acid formed by the oxidation of the sulphur, the removal of the iron by ether is far from complete. The sulphuric acid must be separated from the iron by an ammonia separation so that a solution containing only chlorides may be obtained. There is almost always some slight loss of solution in the treatment with ether in the separatory funnel, but any error from this source becomes negligible if the bulk of the nickel is first separated by ammonia.

After agitating, the funnel is allowed to stand a few minutes and the water solution is drawn off into a second funnel. The ether solution is washed twice with a few cc. of hydrochloric acid (sp. gr. 1.10), the washings being caught in the second funnel. Mr. Sargent contents himself with one ether treatment but we have always found it advisable to remove the iron still remaining with the nickel by a second agitation with 40 cc. of ether. The second operation is carried out in the same way as the first.

The aqueous solution and washings are run into a beaker, the dissolved ether is expelled by boiling, bromine water is added until the solution is strongly colored, and the iron, aluminum and any manganese present are separated by adding ammonia to alkalinity and boiling. If the ether treatment has been properly carried out, a mere trace of iron remains with the nickel and the precipitate may be caught on a 9 cm. paper. The precipitate obtained as above is dissolved in a little hydrochloric acid, bromine is added, and the precipitation with ammonia is repeated. The combined filtrates and washings are added to the casserole containing the now concentrated filtrate from the first ferric hydrate precipitate. The contents of the casserole which now contain all of the nickel in the ore are concentrated to 100 cc. or until ammonium chloride begins to separate. Fifty cc. of concentrated nitric acid are added and the solution is slowly boiled down almost to dryness. In this way the ammonium chloride is entirely destroyed. Ammonium nitrate is unchanged; hence the necessity for avoiding an excess in the oxidation of the ferrous iron. We are now able to concentrate the solution to a volume of a few cc. without the separation of any salts. Ten cc. of concentrated sulphuric acid are added and the casserole heated until dense fumes appear and the nitric acid is entirely

expelled. After cooling, dilute with 100 cc. cold water, boil, rinse into the high beaker used for electrolytic determinations, neutralize with ammonia, and add 25 cc. in excess. Dilute to 200 to 250 cc., insert the spiral and the weighed platinum cylinder, and electrolyze with a strong current,—we have used 1.2 amperes. The precipitation of the nickel is generally complete within three hours.

The separation of iron and nickel by ether has not as yet been used in the analysis of nickel ores, or mattes. It is unequaled for cleanliness, rapidity, and accuracy, and deserves the first place among the many methods proposed for the separation of iron and nickel.

The ammonia separation has proved particularly untrustworthy in our hands. Three and even four separations fail to remove the nickel, even if the acid solution containing the iron be poured into water containing an excess of ammonia.

The ready means afforded for destroying almost unlimited quantities of ammonium chloride by boiling down with an excess of nitric acid is not new, having been suggested long ago by Lawrence Smith in connection with his well-known method for alkali determinations. Yet it has been strangely neglected and we believe has never been used in the analysis of nickel ores, where it is particularly useful as it enables us to avoid the troublesome and inaccurate separation of the nickel as sulphide.

The solutions to be tested for nickel, ordinarily obtained in analysis, are choked with ammonium chloride, which prevents the concentration of the solution and necessitates the preliminary separation of the nickel from a dilute solution of sulphide. The difficulties in the way of precipitating and washing nickel sulphide without loss in the filtrate or washings are too well-known to need repetition.

In some analyses made by the author before his adoption of the ether method it was necessary to test for traces of nickel in several samples of steel. At least 5 grams had to be taken and the ammonium chloride accumulating in the filtrates from the ammonia separations of the iron was so large in amount that concentration to a bulk in which ammonium sulphide would reveal nickel was out of the question. But by boiling down slowly, with copious additions of nitric acid, it was possible to

destroy all the ammonium chloride and to finally test for nickel in a volume of some 15 cc. under ideal conditions.

The ether separation, as based on the solubility of ferric chloride in ether under the above conditions is, in all probability, not restricted to the determination of nickel or aluminum, but may possibly be applied in the separation of small amounts of zinc from iron. The separation of uranium and iron by ammonium carbonate and sulphide is far from satisfactory if the uranium be small in amount. Possibly in this case as well, the ether treatment may result in a decided improvement.

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LABORATORY METHOD FOR THE CONTINUOUS AND UNIFORM GENERATION OF ACETYLENE, AND FOR ITS PURIFICATION.

BY J. A. MATHEWS.

FOR most purposes in which it is desired to employ a stream of acetylene, no purification is necessary, provided the gas has been properly generated from the usual quality of commercial carbide now being produced. Analyses from various sources show that the impurities in acetylene from this source rarely amount to 1 per cent. and a good part of this is likely to be nitrogen. The combined amounts of hydrogen sulphide, hydrogen phosphide, and ammonia seldom exceed 0.2 per cent. In order that the amount of impurities may be as small as possible it is necessary that the gas be produced in the cold. This cannot be done when water is allowed to drip slowly upon the carbide, and furthermore this method causes the gas to be given off spasmodically and the lime residue often bubbles or froths to such an extent that solid matter in considerable amounts may be carried over with the gas. In obviating all these difficulties the following method has proved successful.

The fragments of calcium carbide are placed in a wide-mouthed bottle. They may, with advantage, be suspended in a basket of coarse wire netting, which will keep the carbide away from the

lime residue, and also allow it to be withdrawn at any time. The carbide is covered with an abundance of absolute or 95 per cent. alcohol, and the bottle closed with a two-hole stopper. Through one hole water can be led from a reservoir bottle, and in the other an outflow tube is fitted. If 95 per cent. alcohol is used, the water therein serves to start the generation of acetylene and to expel the air from the apparatus. If, now, water be added drop by drop it comes slowly into contact with the carbide and a steady production of acetylene results. Unless the amount of alcohol present is very small and the rate of generation very rapid, no material rise in temperature ensues. After the addition of water has been stopped, the evolution of gas may be allowed to proceed until the bubbling ceases; the alcohol may then be decanted from the residue and distilled, and, rejecting the first few cubic centimeters, the rest of the distillate will be nearly absolute alcohol.

If it is desired to purify the acetylene, any one or more of several methods may be employed. No single purifying agent which has as yet been advocated, meets all the requirements. For general convenience and thoroughness the following combination of methods is suggested:

The acetylene generated as described above is passed into a solution of 15.6 parts of crystallized copper sulphate in 100 parts of water, to which is added 5 parts of dilute sulphuric acid,[1] 1 volume of sulphuric acid to 4 volumes of water. This solution, besides retaining any vapor of alcohol and also the ammonia and hydrogen sulphide, is especially useful for absorbing hydrogen phosphide. As an additional safeguard the acetylene is next passed through one or two towers filled with coarse bits of pumice stone which have been saturated with an acetic or sulphuric acid solution of chromic acid;[2] or, in place of a second tower, a strong sulphuric acid solution of chromic acid may be used. By this means any of the three chief impurities, which might escape absorption in the copper sulphate solution, will be completely oxidized. A small amount of these purifying materials will serve for a large volume of gas, and the acetylene should issue both dry and pure and possessing a faint and agreeable odor.

[1] Hempel and Kahl : *Ztschr. angew. Chem.*, **53**, 1898.

[2] Ullmann : *J. für. Gasbeleucht*, **42**, 198, 374 (1899).

A return of the strong, irritating odor indicates that the purifiers have become exhausted.

The purification of acetylene by means of moist chloride of lime or sodium hypochlorite, as suggested by Odernheimer[1] and Lunge[2] or as modified by Wolff[3], is impracticable because of the instability of the solutions and because chlorine and chlorination products of acetylene are produced, which must then be removed by lime. Frank's method,[4] using strongly acid solutions of copper or iron chloride, does not seem very efficient, nor is the employment of bromine as a purifier convenient for laboratory use. The combination of Hempel's and Ullmann's methods seems to meet all the requirements and is easily and conveniently arranged.

THE CARBIDE OF GOLD.

BY J. A. MATHEWS AND L. L. WATTERS.

EXPLOSIVE compounds resulting from the action of acetylene or coal-gas upon alkaline solutions of cuprous, argentous and mercuric salts have been known for many years. These compounds are for the most part flocculent precipitates which retain water with more or less tenacity, and at temperatures which will render them anhydrous they are apt to explode violently. The earlier investigators of these acetylides did not recognize them as true carbides and their analyses show the presence of hydrogen and oxygen, which are reported as constituent atoms of the molecule. Berthelot,[5] who did a great deal of work upon acetylene derivatives, speaks of copper acetylide as "cuproacetyloxide," and gives it the formula $(C_2Cu_2H)_2O$. Reboul[6] gives silver acetylide as $(C_2HAg)_2 + Ag_2O$ and Blochmann[7] gives respectively, $C_2H_2Cu_2O$ and $C_2H_2Ag_2O$. All of these might better

1 *Chem. Ztg.*, **22**, 21.

2 *Ztschr. angew. Chem.*, 651 (1897).

3 *Chem. Ztg.*, **22**, 281; Wolff treats the gas first to remove ammonia and then with hypochlorite, thus eliminating the danger of forming nitrogen chloride, which he says is possible.

4 *Ztschr angew. Chem.*, 1050 (1898).

5 *Ann. chim. phys.* [4], **9**, 425.

6 *Compt. rend.*, **54**, 1229.

7 *Ann. Chem.* (Liebig), **173**, 176, 177.

be written C_2Cu_2 or C_2Ag_2 plus more or less water. Miasnikoff[1] gives silver acetylide as $C_2H_2Ag_2$. Keiser[2] showed, however, that when properly dried these two acetylides are simply C_2Ag_2 and C_2Cu_2, and later[3] produced mercuric acetylide, HgC_2, which is also hydrated at the time of its formation.

Berthelot[4] seems to be authority for the statement which appears in a number of old chemical works, but for which these do not give him credit, that by passing acetylene through aurous thiosulphate, a yellow explosive precipitate is formed. He gives no analyses of the product and does not give any suggestions as to its probable constitution.

We have recently investigated this interesting compound, which proves to be analogous to the copper and silver compounds, its formula being aurous carbide, Au_2C_2.

In the preparation of aurous sodium thiosulphate we followed the method of Fordos and Gélis.[5] Pure auric chloride was dissolved in 50 parts of water; 3.2 parts of sodium thiosulphate were dissolved in the same amount of water. The solution of gold was added to the thiosulphate very slowly and with constant stirring. A slight odor of sulphur dioxide was noticed and a little sulphur separated.

The solution was filtered and the sodium aurous thiosulphate was precipitated with absolute alcohol. It was not recrystallized. The principal reaction is said to be

$$8Na_2S_2O_3 + 2AuCl_3 = 2Na_3Au(S_2O_3)_2 + 2Na_2S_4O_6 + 6NaCl.$$
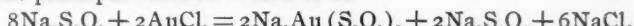
This compound forms a colorless precipitate, very soluble in water but insoluble in alcohol. To form aurous carbide an aqueous solution of the sodium aurous thiosulphate is made strongly alkaline with ammonia and a slow stream of acetylene passed through. The solution remains colorless for a short time and then becomes yellow and finally a yellow flocculent precipitate appears. In this respect it differs from silver and copper carbides, which form almost instantly and hence are used to test for the presence of minute quantities of acetylene. The precipitate is filtered off, washed with water and alcohol and dried in a desiccator over sulphuric acid.

1 *Ann. Chem.* (Liebig), **118**, 330.
2 *Am. Chem. J.*, **14**, 285.
3 *Ibid.*, **15**, 535.
4 *Ann. chim. phys.* [4], **9**, 425.
5 *Ibid.*, [3], **13**, 394, 1845.

Properties.—When thoroughly dried, the carbide of gold is highly explosive either upon rapid heating, by a blow or even by brushing with a camel's hair brush. The explosion generates sufficient heat to produce flame and the gold is left in an extremely finely divided condition and black. Carbide of gold is easily decomposed by hydrochloric acid giving acetylene and leaving a black residue of aurous chloride. The presence of acetylene was shown by passing it into ammoniacal silver nitrate, in which it produced silver acetylide. The aurous chloride was tested by boiling, which gave auric chloride and metallic gold. By boiling gold carbide with water it is decomposed into its constituents, no acetylene being produced. Cupric sulphate and neutral ferric chloride do not decompose it in the cold; when anhydrous it becomes darker in color and of a brown tint and if heated very gradually decomposes without explosion. This fact was made use of in the determination of gold. The sample to be analyzed was heated in the air-bath very slowly until a temperature of 180° to 200° was indicated, and then ignited in the flame of a Bunsen burner. The black mass becomes yellow by the burning off of the carbon and annealing of the gold. The analyses resulted as follows:

	Weight of sample.	Gold found.	Gold. Per cent.	Theory for Au_4C_2.
I	0.029	0.0273	94.14	94.25
II	0.0174	0.0164	94.25	94.25

One sample of aurous carbide after two days in the desiccator lost no weight at 100° C. nor was loss experienced on renewed heating up to 120° C. Another sample that had not stood so long over sulphuric acid lost 0.0004 gram at 100°. By rapid heating in the air-bath explosions were obtained at various temperatures from 83° to 157° C. No attempt was made to secure especially uniform heat at all parts of the air-bath, but the thermometer bulb was in all cases very close to the dish containing the explosive compound. It seems then that the rate of heating has most to do with effecting the decomposition of gold acetylide. The violence of the explosion was shown by several unexpected explosions. In one case about 15 or 20 milligrams of the substance were on a watch-glass. In trying to remove a small fragment with the point of a knife, the whole

mass exploded with a sharp report and the watch-glass was broken into a score of pieces.   In another instance while brushing some of the carbide from a filter-paper with a camel's hair brush into a dish, the particles adhering to the paper exploded with a loud report and flame and the filter-paper was badly torn but the bulk of the material, which was not over an inch or two away, was not exploded by the concussion.   The same fact was noted in the first explosion above in which case the watch-glass was standing beside a crucible containing quite a large amount of dry gold carbide.

No other aurous solutions were tested with a view to obtaining gold carbide.   From auric chloride in aqueous solution metallic gold is precipitated by acetylene.

A solution of auric chloride made alkaline with potassium hydroxide does not give a precipitate under similar conditions, nor does an aqueous or ammoniacal solution of potassium auric cyanide give a precipitate when acetylene is passed into it.

THE NATURE OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SALTS.

BY F. P. VENABLE.

IN a recent number of this Journal[1] Whitney has reported further work upon this problem and at the same time criticized an article by Venable and Miller which had previously appeared upon the same subject.[2]   As Mr Miller is no longer at work with me and I was, in the main, responsible, for the presentation and discussion with which Dr. Whitney finds fault, my name appears alone in this reply.

Whatever disinclination I may have felt to accept as final the previous efforts at determining the presence of free sulphuric acid in the green solutions, I can have none as to this recent admirable and conclusive direct determination of the acid by Whitney. It is, of course, of little importance to explain why an opinion was formed, unless truth is advanced by such explanation.   I shall therefore only refer to two or three of the facts stated by Whitney as sufficient to convince one that free sul-

1 This Journal, 21, 1075-1084.

2 Ibid., 20, 484-496.

phuric acid is present.   I do this because I cannot verify them as facts.

1. Dr. Whitney states that the green solutions are acid to the usual indicators.   We could draw no conclusions as to the difference between the solutions from this because both violet and green solutions are thus acid.   This statement was made by us in the original article and has been carefully verified by me since reading Whitney's article.   It is also supported by the experiments of Baubigny and Pechard.   Furthermore, the mere fact that barium chloride is prevented from precipitating all of the sulphuric acid in the green solution cannot be taken as proving the presence of free sulphuric acid.

2. Whitney cites Recoura as stating that the " distillation of the green solution results in an acid distillate, while the violet salt may be heated above 100°C. without loss of acid."   My experiments failed to verify this.   I took 15 grams of the alum and dissolved it in 200 cc. of distilled water.   This was then carefully distilled from an ordinary distilling flask connected with a condenser and the distillate treated in successive portions of 50 and 25 cc. until only about 25 cc. were left, without finding any acid. Beyond this point the temperature began to rise, portions splashed upon the sides became overheated, and acid distilled over.   This was repeated with chromium sulphate with the same result.   It was also repeated with ordinary potash alum with the same result.   As the solution became very concentrated the temperature rose, portions were splashed upon the hot sides and acid distilled over.   Lastly, it was repeated with 5 cc. of sulphuric acid in 200 cc. of water and no acid distilled over until most of the water had been driven off and the temperature had risen above 100°C.   Manifestly this experiment of Recoura's can throw no light upon the presence or absence of free acid.

3. Krüger's statement that alcohol poured in a layer over the green solution takes up acid (something that gives an acid reaction) from the solution is only part of the truth for alcohol will do precisely the same thing when poured over the violet solution. In the course of a few hours the reaction is quite perceptible from both solutions.   There is no change apparent in the color of the violet solution after four or five days' standing under the layer of alcohol.

After weighing the evidence then at hand I reached the conclusion that a satisfactory explanation of the change could scarcely be deduced from these and the other experiments.

And they did not seem to me to justify the construction of an equation and an elaborate formula for a hypothetical substance which was assumed to cause the green coloration, even if the presence of the free acid should be granted.

The exception is well taken by Whitney to our experiment with the decinormal solution of ammonia and explains a result which greatly puzzled us in the interpretation of our later work. We scarcely knew what value to attach to the experiment and so merely stated that "these experiments therefore agree with those of Baubigny and Pechard, but are at variance with the conclusions of the other authors mentioned." The agreement was, of course, only to the extent that "both solutions are acid" and that was all that was claimed for the experiment.

It seemed to us necessary to get under hand for analysis the body which gave the green coloration before any formula could be established for it.   We therefore abandoned what we styled "indirect methods giving results capable of other explanations." We thought it more material to secure this body than to settle the question as to whether free acid or an acid sulphate was formed.   Certainly any other line of research would always leave the body in question hypothetical.   Hence in the latter part of the paper[1] the sentence occurs, "as the alcohol left is decidedly acid it must contain either free acid or an acid sulphate" and there was no further effort at settling this point.

The method which most commended itself to us for securing this compound was precipitation by means of alcohol.   In this precipitate, in the case of the alum, we obtained the potassium sulphate along with the chromium compound and this blinded us to the true formula.   A recalculation of the results of Mr. Miller's analyses, eliminating the potassium sulphate, and taking the mean of the experiments, gives as the ratio of the chromium to SO_4, 18.23 : 41.62.   Now the ratio, calculated for the formula $Cr_4O.(SO_4)_4.SO_4$, is 18.23 : 41.99.   Having then the direct determination of the free sulphuric acid from Whitney's last experiments and the gravimetric determination of the chromium

[1] This Journal, 20, 496.

and SO_4 in the basic chromium sulphate from Miller's analysis, there can no longer be any reason for not accepting the equation given for the change :

$$2K_2SO_4.Cr_2(SO_4)_3 + H_2O = 2K_2SO_4 + Cr_4O(SO_4)_4.SO_4 + H_2SO_4.$$

The conclusion drawn in the article by Miller and myself was conservative and still stands ; namely, that the color of the green solutions was due to the formation of basic salts of chromium, green and uncrystallizable, thus confirming the explanation first suggested by Berzelius. To this must now be added that this formation is accompanied by the liberation of a portion of the combined acid, in the case of the alum corresponding to one-half of the total.

ON THE DECOMPOSITION OF NICKEL CARBONYL IN SOLUTION.

BY VICTOR LENHER AND HERMANN A. LOOS.

IT has been shown by Berthelot that nickel carbonyl in contact with moisture suffers decompositions of a more or less complex character. When nickel carbonyl is mixed with water according to Berthelot[1] there is formed a green compound which consists of hydrate of the oxide free from carbon. A portion of the nickel carbonyl at the same time escapes and is oxidized in moist air to a whitish compound. This same white compound Berthelot prepared in larger quantity by the slow oxidation with air and found it to contain 5.3 per cent. carbon, 53.3 per cent. nickel oxide (NiO), and 40.1 per cent. water.

Mond[2] considers the green body formed when nickel carbonyl is exposed to damp air to be a carbonate of nickel of varying composition.

The deportment of nickel carbonyl in solution is different from that in the pure condition or as a gas, as is seen, for example, from the fact, that it will decompose in solution at $60°$, whereas in the gaseous condition, it will not decompose until about $150°$.
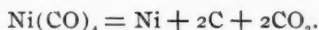
1 *Compt. rend.*, **112**, 1343 ; **113**, 679.
2 *Chem. News*, **64**, 108 ; also *J. Soc. Chem. Ind.*, **11**, 750.

In gaseous condition, heat decomposes it simply, into nickel and carbon monoxide.

$$Ni(CO)_4 = Ni + 4CO.$$
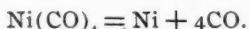
In solution the action takes a different form and may be represented as follows :

$$Ni(CO)_4 = Ni + 2C + 2CO_2.$$

It would not be surprising then to find that the solution would act differently than the pure substance, under the action of moisture or oxidation.

While working with nickel carbonyl dissolved in various organic solvents, such as chloroform, benzene, toluene, etc., it was found that the solutions on standing suffer decomposition with the formation of a green precipitate ; this was probably due to the presence of more or less moisture, either in the solvent or in the surrounding atmosphere. That the precipitate is produced by the action of moisture is evidenced by the fact that the decomposition is more rapid when the solution is exposed to the air and still more rapid when moist air is bubbled through the solution.

A solution of nickel carbonyl will, after standing, suffer decomposition with the formation of a green to a brown gelatinous precipitate. In appearance, this precipitate is similar to that obtained by the action of water or moisture on pure liquid nickel carbonyl.

The precipitate formed from various solvents has been studied with a view of determining if possible its composition. The substance is evidently of very complex nature and is undoubtedly an oxidation product. When a solution of nickel carbonyl in acetone or chloroform is allowed to stand, a green gelatinous precipitate forms in a few hours. After a greater length of time the precipitation becomes complete, and on filtration, no nickel can be found in solution. This same decomposition takes place but more slowly in benzene, toluene, and methyl alcohol. The precipitate is colored light green to dark brown according to the solvent used, and according to the small amount of iron carbonyl which frequently contaminates the nickel carbonyl. The deportment of the solution in ethyl alcohol is peculiar. If this solution is mixed with an equal volume of water, a clear solution is

first obtained, but in a few minutes, it gelatinizes to a green translucent mass. This substance settles very slowly. On filtering off the precipitates and carefully drying, all assume a greenish color. Examination of this precipitate indicates that it is a decomposition product which contains nickel carbonyl and nickel hydroxide.

Analyses of the substance obtained from toluene gave the following results :

	Calculated for $Ni(CO)_4.2Ni(OH)_2.4H_2O$.	Found.	
		I.	II.
Carbon	11.19	11.66	11.38
Hydrogen	2.80	2.95	2.97
Nickel	41.26	42.82	42.68

As different samples gave results which differed slightly, it appears that the composition of the substance varies slightly as is apt to be the case in an oxidation product. A precipitate from benzene was found to contain 42.09 per cent. of nickel, while one from chloroform contained 42.81 per cent.

The precipitate carbonizes with sulphuric acid while with dilute acids carbon dioxide is evolved. Sodium or potassium hydroxide attacks the precipitate and apparently removes a portion, since after treatment with one of these alkalies and thoroughly washing, acids will no longer produce effervescence. Potassium iodide is without action ; potassium cyanide dissolves it to a brown solution. It is insoluble in chloroform, benzene, toluene, petroleum ether, alcohol, acetone, methyl alcohol, or ether. Ammonium sulphide converts it to the black sulphide of nickel. Although the formula calculated for comparison with the analyses does not account for the evolution of carbon dioxide with an acid, yet this can be explained by the fact that carbon dioxide is invariably a result of the decomposition of nickel carbonyl in solution.

ERRATUM.

In the December issue (1899), on page 1145, in the fourth line of table, for "calcium chloride" read "chloride of lime (bleaching powder)."